DJV

FINAL REPORT

PROJECT NO. A-330

DEVELOPMENT OF MONOLITHIC CERAMICS AND HETEROGENEOUS CERAMIC-METAL BODIES FOR AERODYNAMIC APPLICATIONS AT HIGH VELOCITIES AND TEMPERATURES

By

N. E. POULOS, J. D. WALTON, W. T. TEAGUE
and M. D. BOWEN

RESEARCH PROJECTS LABORATORY
U. S. ARMY ORDNANCE
ARMY BALLISTIC MISSILE AGENCY
CONTRACT NO. DA-01-009-ORD-548

1 APRIL 1957 to 31 MARCH 1959

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

FINAL REPORT

PROJECT NO. A-330

DEVELOPMENT OF MONOLITHIC CERAMICS AND HETEROGENEOUS CERAMIC-METAL BODIES FOR AERODYNAMIC APPLICATIONS AT HIGH VELOCITIES AND TEMPERATURES

By

N. E. POULOS, J. D. WALTON, W. T. TEAGUE
and M. D. BOWEN

RESEARCH PROJECTS LABORATORY
U. S. ARMY ORDNANCE
ARMY BALLISTIC MISSILE AGENCY
CONTRACT NO. DA-01-009-ORD-548

1 APRIL 1957 to 31 MARCH 1959

TABLE OF CONTENTS

(Continued)

TABLE OF CONTENTS (Continued)

This report contains 115 pages.

LIST OF FIGURES

(Continued)

LIST OF FIGURES (Continued)

(Continued)

LIST OF FIGURES (Continued)

Page

LIST OF TABLES

(Continued)

LIST OF TABLES (Continued)

I. SUMMARY

At the initiation of this contract the technique for slip casting fused silica was known to exist only for an impure form of silica called Vycor, which is marketed under the trade name of Glascast. Since pure fused silica articles were desired, studies were undertaken to determine the particle size requirement of the fused silica grain that was available and the amount of water, auxiliary binders, and additives needed for producing a casting slip. A slip was developed for fabrication of articles of essentially pure fused silica. Throughout this development, test samples representing major accomplishments in fabricating techniques were evaluated at Redstone Arsenal. The data from Redstone indicated high promise for fused silica as a nose cone material.

Following the development of a satisfactory fused silica slip, experiments were conducted to determine if special properties could be obtained in fused silica articles by addition of small percentages of other materials; for example, graphite and copper were added to fused silica slips and a heterogeneous body was successfully cast with no loss in thermal shock resistance or lowering of the melting point.

Other materials were added to fused silica bodies which lowered the melting point of the silica and decreased the viscosity of the resulting melt and thus increased the ablation rate. Portland cement or calcium aluminate cement were used with various percentages and particle sizes of fused silica grain (aggregate) in the development of easily workable troweling or aggregate castable mixes. Preliminary tests of these troweling mixes at Redstone Arsenal indicated that the ablation rate may be increased depending upon the type and amount of cement used.

Thus, compositions could be tailored for specific applications. It is also feasible to fabricate articles in which the additive to the final silica article can be graded from a relatively high content at one surface to a low content or complete absence at the other surface. Other properties of articles slip cast from fused silica which were observed during this work are as follows:

1. Low shrinkage -- as low as 0.3 per cent total drying and firing shrinkage
2. Easy machinability using grinding techniques
3. High degree of surface replication permitting close tolerances with little or no machining required. Threads have been slip cast in the back of nose cone specimens for the 1/4HT burner.

A feasible means of attaching the finished fused silica article to conventional substructures was investigated. Both organic and inorganic cements and adhesives were tried. An adhesive such as Shell Epon Adhesive VI appeared to be satisfactory.

A small oxyhydrogen rocket motor test facility in the Ceramics Branch of the Georgia Tech, Engineering Experiment Station, was evaluated for possible use as a preliminary test device for screening various compositions to be tested by Redstone Arsenal's 4HT burner. The maximum ablation rate for this device was approximately one-half the ablation rate of the 4HT burner.

An apparatus for measuring thermal conductivity in excess of 1600° F was constructed. The design of the guard-ring type unit used in the American Society of Testing Materials' C177-45 was modified to extend the temperature range to 2000° F. These design modifications resulted in a device not requiring cumbersome equipment for measurements of thermal conductivity of various refractory-type materials with a maximum error of ±5.6 per cent.

During the second year of this contract a nose cone, which was designed as an extended projection of the nose cone tips that are tested on the 164HT burner at Redstone Arsenal was fabricated and tested successfully. This tip was extended to provide a nose cone with an overall height of 25 inches and a base diameter of 19 inches. The relative ease of fabrication of this nose cone, by slip casting fused silica in plaster molds, has led to the conclusion that there are no limitations, due to size alone, to the fabrication of fused silica articles.

This report is a final summary of 2 years' work under Contract No. DA-01-009-ORD-548.

II. PURPOSE

The purpose of Contract No. DA-01-009-ORD-548 is the development of high temperature resistant materials for aerodynamic application at high velocities and temperatures.

III. INTRODUCTION

Rocket development has progressed to the point where re-entrance velocities have become a serious problem. The high temperatures resulting from the high re-entry velocities require that some means be provided to protect the nose section of a re-entry vehicle from destruction.

Ceramic or ceramic-metallic compositions for use as re-entry materials have been of primary interest. However, previous experiences with ceramics for such applications indicated that, of the properties most desirable of a nose cone, the most difficult to obtain was thermal shock resistance. Our past experience with fused silica at Georgia Tech led to a serious look into the possibilities of using fused silica as the major, if not the only, constituent of a ballistic nose cone.

The primary objective of this contract was to produce a ceramic nose cone which would withstand the severe thermal shock provided by re-entry conditions. Although many ceramic materials have higher melting points than fused silica, none possesses the thermal shock resistance of this material. Further, fused silica provides a very viscous melt at its melting point (3100° F), and thus appeared to offer some hope of surviving re-entry, although surface temperatures in excess of 5000° F would be anticipated. Three factors combine to make this possible:

1. Short duration of re-entry
2. High insulating value of cast silica
3. Relatively high heat capacity

Georgia Tech's work with fused silica began in the fall of 1956, with the objective of developing a permanent foundry mold in which iron as well as other ferrous and nonferrous metals could be cast. Finely ground fused silica was suspended in water and subsequently this slurry was poured into a plaster mold of the desired configuration. The plaster mold, due to its porous nature, caused water to be removed from the slurry and resulted in the formation of a cake of silica particles next to the mold wall. The thickness of this cake was determined by the length of time that the slurry was allowed to remain in the mold. After the desired thickness was obtained, the remaining slurry was poured from the mold and the cake allowed to dry. This cake, which consisted of closely packed silica particles, was then sintered between 1800° F and 2100° F to provide the desired strength.

This technique, by its nature, provided a relatively inexpensive fused silica shape which was required in the foundry mold field. It also provided a means whereby large and intricate shapes could be fabricated from fused silica, which was not possible by the techniques which have been used to construct glasslike articles from silica. Figure 1 compares the two processes. By the older technique, molten silica was poured and worked in graphite or other suitable molds above 3100° F until the desired piece was obtained. This was necessarily limited to relatively small and simple shapes and, due to these conditions, the pieces produced were quite expensive. Therefore, fused silica has generally been associated with high quality chemical glassware and precision optics, where cost was of no real concern and large and intricate shapes were seldom required. Conversely, the slip casting of fused silica is accomplished by using readily available and inexpensive fused silica

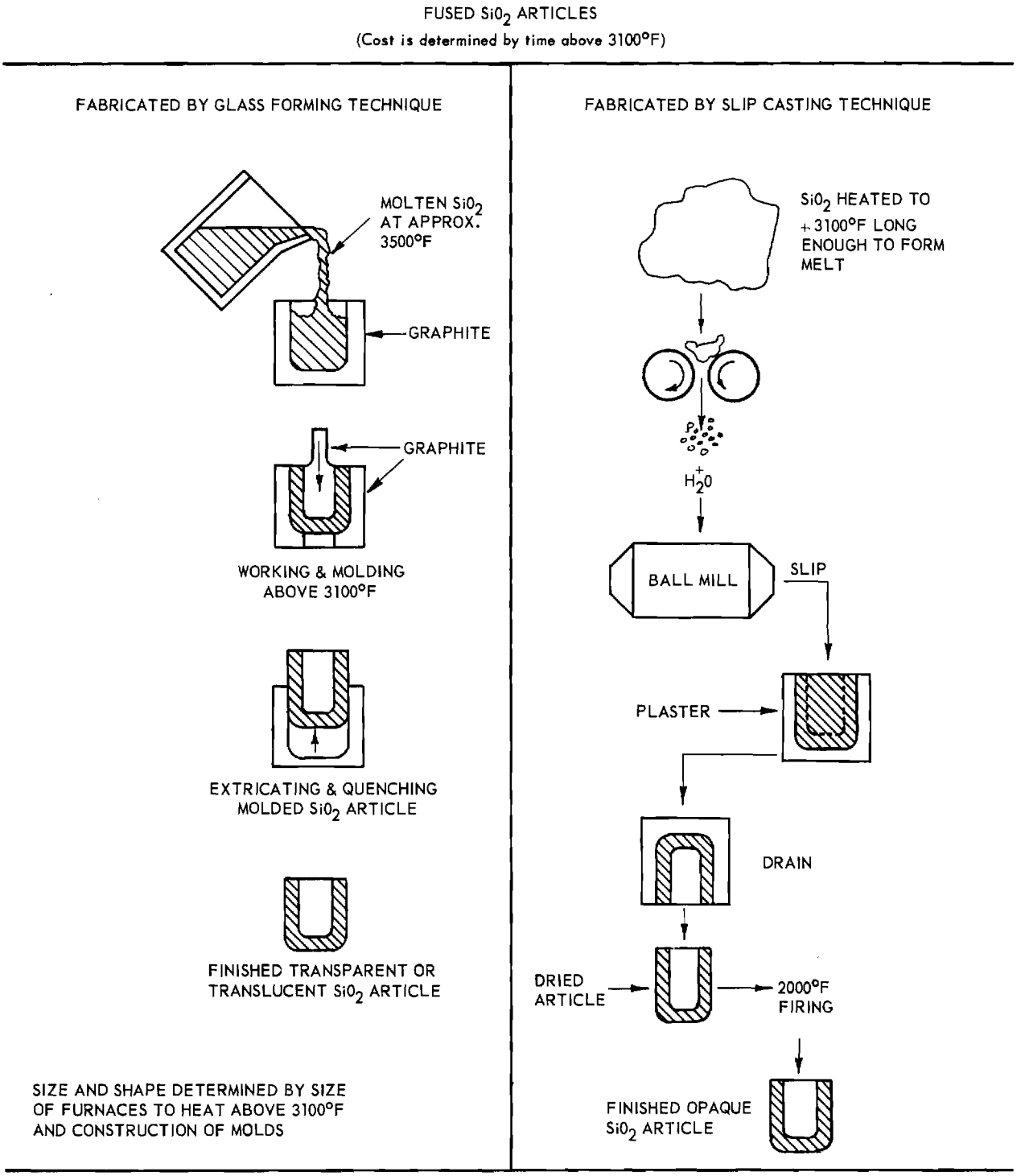


Figure 1. Diagram Showing Fabrication Processes for Manufacture of Fused Silica Articles.

which has been heated above 3100° F only long enough to melt the silica. The material is then crushed, mixed with water and pulverized in a ball mill to provide a slurry or slip of fine fused silica particles suspended in water. The slip is then used as described previously. This technique provides articles which differ from the glasslike fused silica articles only in that they are opaque and generally porous. The strength of slip-cast articles is approximately one-fourth to one-half that of the clear glass but their insulating value is much better. Also, being opaque, they do not transmit radiant energy nearly as well as clear glass.

Probably the greatest advantage to be obtained from the slip-casting process is the ability to provide large shapes of fused silica. Experience to date has indicated no foreseeable size limitations. Slabs 8 feet long, 4 feet wide, and 6 inches thick have been fabricated on a semi-production basis by the company which provides the Station with the fused silica slip.

Preliminary tests under this contract indicated that our first samples of slip-cast fused silica would possess the thermal shock resistance desired in a nose cone material. At this point, other properties possessed by fused silica were examined more closely in light of present and future requirements for nose cones.

Future requirements for high velocity re-entry would suggest that a material with a lower ablation rate than the fiberglas plastic currently in use should be sought.

IV. EXPERIMENTAL WORK

A. Casting Fused Silica Grain

1. Grain and Binders

This section covers the work with mixtures of fused silica grain and various binders--colloidal silica, Hi-Early Portland cement and Lumnite (calcium aluminate) cement.

Studies were made to determine the effect of colloidal silica, which was used as a binder, on the strength of a body made of amorphous silica grain. The amorphous silica selected was -100 mesh as milled, of which approximately 50 per cent was -325 mesh. This silica was blunged with five different commercial grades of colloidal silica dispersions forming a semislip mixture. Special techniques had to be developed for casting test bars, since the colloidal silica used as a binder in these preliminary studies promoted adherence between the ware and the plaster mold, in which it was cast. It was decided that small wax-impregnated cardboard boxes of the desired shape would serve as the molds into which the silica suspensions would be poured. These boxes served the purpose very well.

Test bars were cast to determine modulus of rupture under the following conditions:

1. Bars dried at 230° F and fired at 1800° F for 30 minutes.
2. Same as 1., above, but soaked in colloidal silica after firing and refired at 1800° F for 30 minutes.
3. Bars dried, soaked in colloidal silica and then fired at 1800° F for 30 minutes.

Of these tests, the bars of 1. were by far the weakest, with 2. being a little stronger than 3.

A preliminary study was made of the effect of particle size distribution on the strength of bars cast from amorphous silica. Blends of the following particle sizes were evaluated:

-100+150 mesh

-150+325 mesh

-325 mesh

All test bars were cast from a suspension of which 8 per cent of the solid content was colloidal silica supplied from the 30 per cent colloidal silica dispersion. The bars were dried at 230° F and fired at 1800° F for one hour. Each bar was then soaked in a 30-per-cent-colloidal-silica dispersion, dried and refired at 1800° F. This soaking and refiring process was repeated four times.

Bars with modulus of rupture values in excess of 1500 psi resulted from the material exhibiting a particle size distribution within the following ranges:

Percentage	Mesh
15 to 40	-100+150
30 to 55	-150+325
30 to 55	-325

The following technique was successful in casting fused silica articles in plaster molds:

1. A 0.2 per cent solution of Keltex was poured into the mold, allowed to stand for 2 minutes and then poured off.

2. A suspension was prepared consisting of 50 parts of -325 mesh amorphous silica, 37.5 parts of 0.5 per cent solution of Keltex, and 12.5 parts of 1.0 per cent solution of Carbopol 934.

3. The above suspension was poured into the mold and allowed to remain until the desired cast thickness was obtained. The remainder of the suspension was then poured from the mold.

4. The cast piece was allowed to dry and was then removed from the mold.

Although the primary purpose of this study was to develop a means of slip casting in order to form relatively thin-walled objects, it was found that Step 1. above provided a thin film on the surface of the mold which prevented colloidal silica from adhering to the plaster and interfering with mold release. Thus, the early problem of mold release was overcome.

The firing of this material had been carried out at 1800° F, a temperature to which amorphous silica could be subjected for any extended period of time without the formation of cristobalite. It was thought, however, that sufficient strength might be developed below this temperature. Several test compositions were fired at 100° F intervals over the range of 1100° to 1800° F. This study indicated that no significant additional strength was developed in firing above 1100° F.

It was later determined that firing between 1100° and 1800° F served to dehydrate the silicic acid which was present, and that the resulting silica film acted as the cement for the silica grains which were the major constituent of the suspensions. By firing above 1800° F, especially in the 2000° to 2100° F range, it was found that small amounts of cristobalite were developed. Since it appears that cristobalite forms on the surface of silica particles, this initial cristobalite development actually improved the strength of the fired piece. Thus, throughout the later phases of this work firing was carried out primarily in this higher temperature range.

Preliminary investigations were initiated to determine the effect of

other possible fused silica binders as a substitute for colloidal silica. The three binder materials considered were as follows:

1. Clay -- a refractory material of which preliminary test data obtained from another project indicated that percentages as high as 20 per cent do not significantly alter the thermal shock resistance of the resulting body.
2. Lumnite cement -- a refractory cement used for insulation.
3. Hi-Early Portland cement -- a Portland cement which develops a high strength with short set times.

Pyrometric cone fusion tests were conducted to determine the effect of varying percentages of these binders on amorphous silica compositions. Figure 2 shows the results of these tests.

Small percentages of Hi-Early Portland cement had the least effect on the fusion points with Lumnite cement having the greatest effect. Preliminary studies indicated that the least strength and thermal shock resistance were obtained where Lumnite cement was used. The use of Lumnite cement was abandoned.

A composition containing 30 per cent Hi-Early cement and 70 per cent amorphous silica exhibited transverse strength of 1000 psi. Ware cast from a mix containing 10 parts Hi-Early, 90 parts -325 mesh amorphous silica grain and 25 parts water exhibited good strength and thermal shock resistance to a thermal quench from 1800° to 80° F.

2. Milled Fused Silica Slip

A ceramic slip may be simply described as a slurry of finely divided particles suspended in a liquid medium, usually water, with the particles so dispersed that they tend to remain in suspension for reasonable periods of

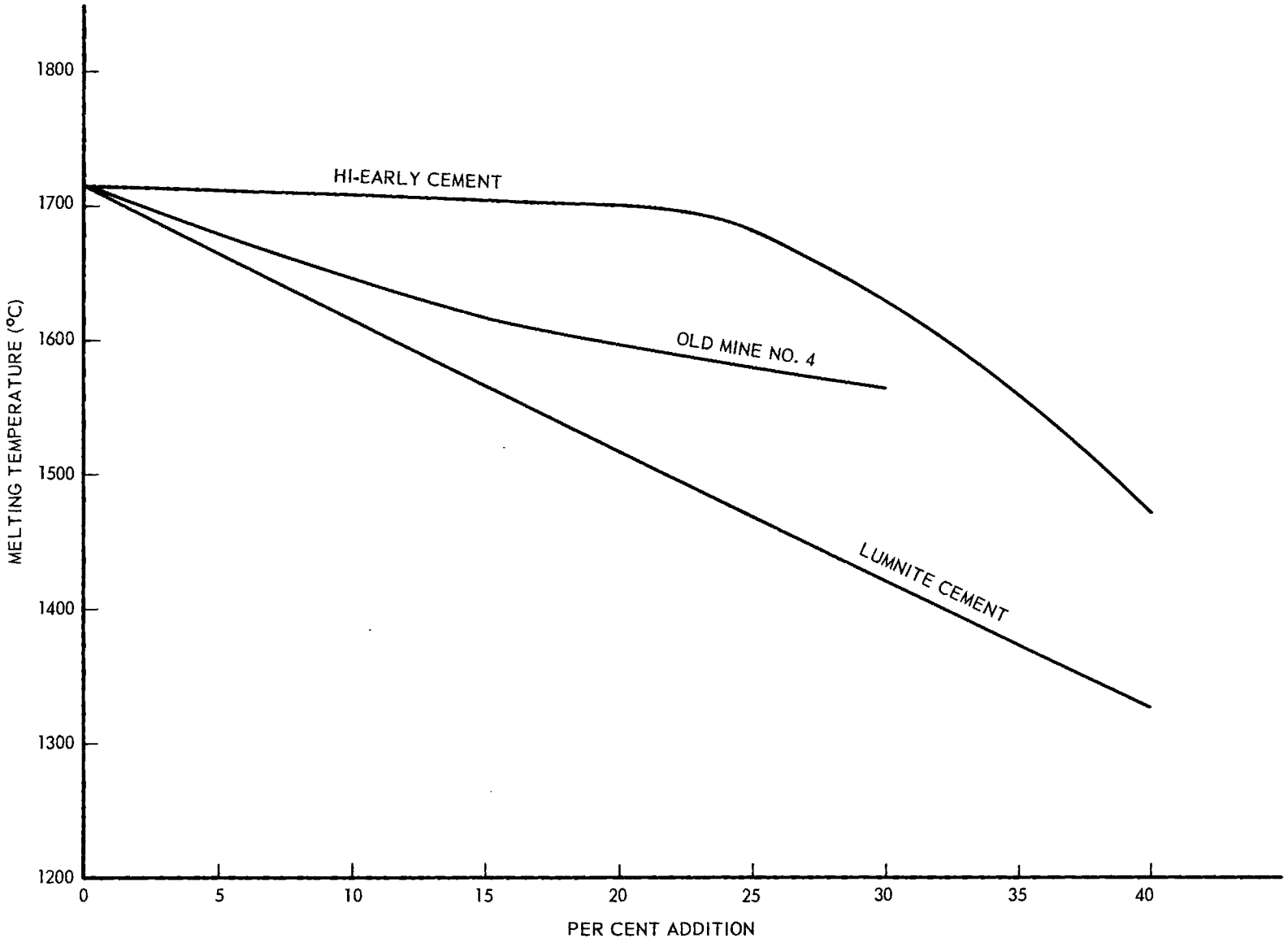


Figure 2. Effect of Additions of Cements and Clay on Melting Point of Fused Silica. PCE Determination.

time. Thin-shelled objects having intricate configurations can be easily formed by casting such a slip in plaster molds. Because of this fabrication ease, attempts were made to prepare a fused silica slip by ball milling fused silica grain. The dispersion of the solids of such a slip by the addition of electrolytes was also investigated.

Various grain sizes and quantities of fused silica, suspending media such as collidal silica dispersions or water, and milling time were studied.

Of the preliminary ball-milling attempts, a slip which was prepared by the following milling method exhibited good casting properties.

(a) 2,000 gm of -30+100 mesh fused silica grain

(b) 800 ml of Ludox HS colloidal silica

(c) 6000 gm of Burundum grinding cylinders

(d) in a one-gallon porcelain mill

(e) milled for 24 hours

Test bars cast with this slip, which were fired at 1800° F for one hour, had transverse strengths of 2000 psi.

A thin-shelled (1/4-inch-thick) nose cone tip was cast with this slip. The nose cone tip was dried at 230° F and fired at 1800° F for one hour, cooled to room temperature, and then filled with a slurry composed of -30+100-mesh fused silica grain and Ludox HS colloidal silica. The nose cone tip was dried and fired at 1800° F for one hour, cooled, soaked in a 30-per-cent-solids dispersion of colloidal silica and refired at 1800° F. Thermal shock failure was not evident in the shell, the fill or the bonding of the cavity-filled material with the shell. No thermal shock failure occurred during five quenching cycles.

From the milling time studies, it was observed that the transverse strength of test specimens cast from the milled material increased as the

milling period was increased. The highest transverse strength, 3620 psi, was observed for a milling period of 48 hours. Excessive milling tended to produce surface crazing of large cast ware. At first, it appeared as though only the ware that was cast from slips containing colloidal silica exhibited crazing; however, it was observed that slips containing no colloidal silica additions, but which were milled in water for a period of time, 168 hours, exhibited surface crazing. This crazing effect was attributed to an excess of fine material (probably colloidal) at the surface of the cast piece.

The dispersion of a slip is usually accomplished by the addition of an electrolyte. Several commercial electrolytes were investigated for their possible use to disperse the milled fused silica slips. Polyfon O, Tennessee Air Extra and TSPP were used as electrolytes in this study. The Tennessee Air Extra exhibited the best dispersing properties. The slip dispersed with 0.2 to 1.5 ml of a 25-per-cent solution of Tennessee Air Extra to 400 ml of an 80-per-cent-solids slip exhibited a viscosity curve which was essentially flat. Its minimum point was 188 centipoise using 0.6 ml of Tennessee Air Extra. The initial viscosity of the slip was 268 centipoise as measured with a Brookfield Viscosimeter.

Investigations were made to determine the effect upon the properties of fused silica slips with a controlled pH. Small additions of acids or bases -- hydrochloric acid or ammonium hydroxide -- were added to the slips and the viscosity was determined. A typical curve showing the effect on viscosity of changing the pH is found in Figure 3. Minimum viscosities were obtained with both the acid and basic slips. This could be expected by studies of other pure oxide slips that also show a minimum viscosity in both regions[1]. One minimum viscosity range of fused silica slips is found in the pH range from 6 to 4.

The slips obtained and untreated generally have pH's that are within this range, thus making it unnecessary to add dispersing agents to reduce the viscosity for most applications. This acid type slip could possibly be caused by the formation of silicic acid during the milling process. Greater affects upon viscosity have been observed with an increase or decrease in the slip density.

The supplier of the fused silica grain which was being used on this work, developed and started manufacturing a fused silica slip with good casting properties. The slip could be purchased in large quantities at a relatively low price. Thus, no additional work on milling of fused silica into a casting slip was performed. This slip is a water-milled slip apparently using colloidal silica as the suspending agent. Although the exact composition is proprietary with the company, the normal particle size distribution is approximately 95 per cent less than 44 microns, with 20 to 30 per cent less than 2 microns remaining in suspension. Unless otherwise specified this is the slip that was used for the majority of the investigations of this work.

3. Additions to Fused Silica Slip

Investigations were made of additives such as clay, powdered copper, iron-tin alloy, graphite, glass fibers, and phosphorus pentoxide to fused silica slips in an effort to develop techniques whereby compositions of fused silica may be tailored to fit some specific requirement of a re-entry vehicle.

Kentucky Old Mine No. 4 ball clay and EPK kaolin were dispersed into slips and added to the fused silica slip in increments of 1, 5, and 10 per cent based on the weight of the solids. From the preliminary investigations it was observed that the 5-per-cent-clay addition improved the casting and fired strength of the fused silica slip. The one-per-cent-clay addition showed no improvement and the 10-per-cent-clay addition was detrimental to

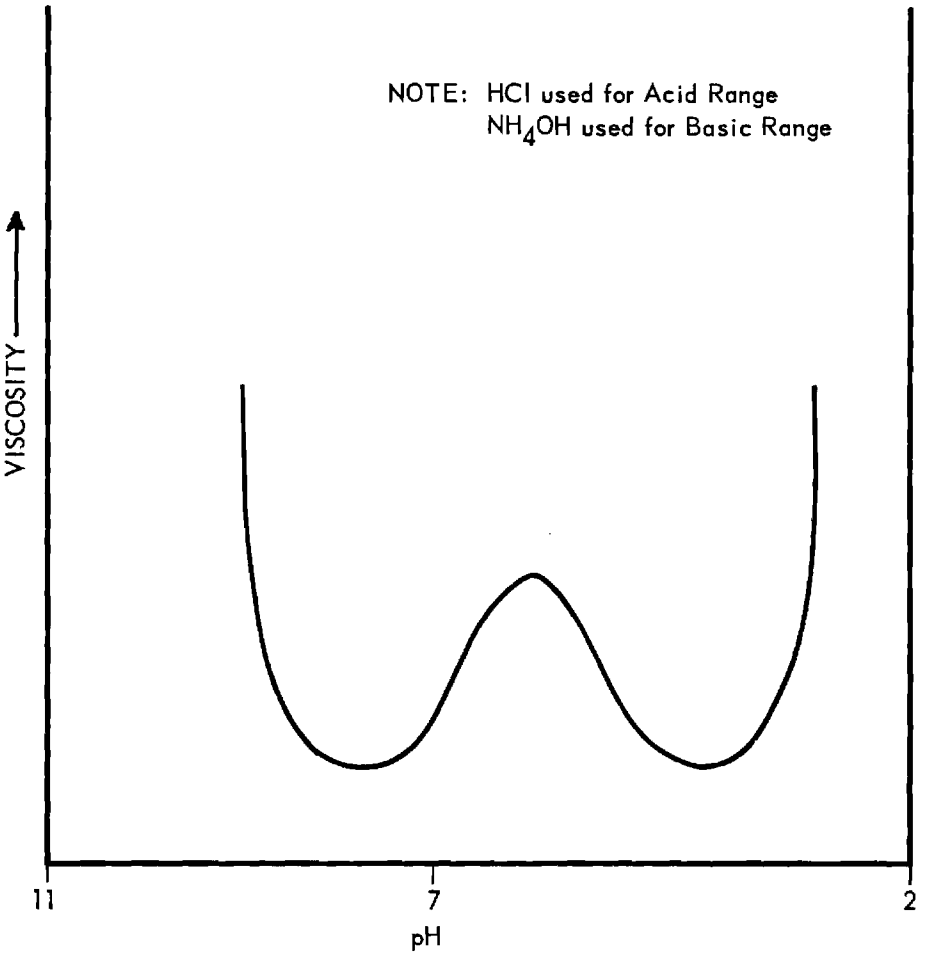


Figure 3. Typical Curve Showing Effect of Slip pH on Viscosity.

both the casting and fired properties of the fused silica slip. Thus, the 5-per-cent-clay addition was investigated in detail. Two firing temperature ranges were studied, 1800° F and 2100° F. The test specimens were fired slowly from room temperature to final heat so that the clay could lose its chemical water slowly.

Table I indicates the effect of the clay addition and firing temperature on the transverse strength of silica ware.

TABLE I

EFFECT OF CLAY ADDITION AND FIRING TEMPERATURE ON STRENGTH OF FUSED SILICA WARE

Fused Silica (%)	EPK (%)	Old Mine No. 4 (%)	Firing Temperature (° F)	Transverse Strength (PSI)
100	-	-	1800	510
95	5	-	1800	1530
95	-	5	1800	1005
95	5	-	2100	2295
95	-	5	2100	3083

The increases in strength of the fired fused silica with the clay additions were attributed to the formation of mullite ($3\ Al_2O_3.2SiO_2$). This small addition of clay did not seem to affect the thermal shock resistance of the fused silica. Thin nose-cone tip shells were thermal shocked from 1800° F to 60° F by immersion in water at 60° F without any failure being observed.

Kentucky Old Mine No. 4 ball clay was calcined at 1130° F and added to the water-milled fused silica slip in increments of 5 and 10 per cent. The purpose of calcining the clay was to remove the chemical water from the clay and eliminate the slow firing-cycle that was necessary when clay was used.

Cast specimens could be fast fired at 1800° F by using calcined clay. The average transverse strength of the 5-per-cent-calcined-clay addition to fused silica slip was 1570 psi and the strength of the 10-per-cent-calcined-clay addition was 1414 psi.

Additions of graphite, copper, and a 60-per-cent-iron--40-per-cent-tin alloy to fused silica slip were made in an attempt to fabricate a graded cross section. The additive was concentrated at the front surface of the cross section and gradually depleted before reaching the back surface. This graded effect was accomplished by casting thin shells from several fused silica slips with varying concentrations of the additives in such a manner as to form a multilayer laminate. Test bars cast from these slips exhibited very poor transverse strengths.

In a further attempt to form a graded cross section, porous fused silica ware was flame-sprayed with powdered copper and the iron-tin alloy using a Metco Thermo Spray gun. The coated ware was then heated in an inert atmosphere, argon, above the melting temperature of the coating but not above 2000° F. It was thought that this heating treatment would cause the coating to infiltrate the porous substrate; however, this attempt was not successful. Microscopic examination of the interface between the coating and the substrate indicated that the metal coating was bonded to the silica grain, that is, wetted the silica grain. Figure 4 is a metallograph showing the interface of the coating with the fused silica substrate. This wetting action may indicate a possible technique for metal-cladding a fused silica nose cone shell.

Additions of fused silica fibers and fiberglas fibers were made to fused silica slip in an effort to determine their effect on the strength of bars made from the resulting mixture. The following compositions were studied:

Figure 4. Metallograph Showing Interface of Flame-Sprayed Copper on Fused Silica. (360x).

(1) 6 gm of 1/2-inch fine fused silica fibers to 500 ml slip,

(2) 15.5 gm of 1/2-inch coarse fused silica fibers to 500 ml slip, and

(3) fused silica fiber cloth, three layers of 4-inch x 4-inch, were placed into slip that had been poured into a 4HT burner plate mold. Test bars were cut from this plate.

All of the above test specimens, including standard test bars, were fired in a sagger, covered with silica, to 2000° F for 2 hours. Low strengths were observed for all of the test specimens. These low strengths were attributed to the test specimens not attaining the desired firing temperature. The strength results were as follows:

Test Specimen	Modulus of Rupture (PSI)
Standard	835
Fine fibers	1000
Coarse fibers	1065
Layers	520

The slip mixtures containing the short fused silica fibers tended to let the slip cast to the outside and a concentration of the fibers in the center was observed. In order to try to correct this tendency test bars of larger volume were prepared from mixes receiving a more thorough mixing using a Hobart N-50 mixer. Table II shows the compositions, mixing time and average transverse strength of two series of test bars fired in a gas kiln to Cone 5 approximately.

Both of the mixes produced weaker bodies than the slip alone, and the fibers still tended to concentrate to the center of the bar.

TABLE II

EFFECT OF FUSED SILICA FIBERS ON STRENGTH OF FUSED SILICA WARE

Sample	Mixing Time (Minutes)	Average Modulus of Rupture (PSI)
(A)-16 gm 1/2-inch fine strains/1000 ml fused silica slip	15	3687
(B)-16 gm 1/2-inch coarse strains/1000 ml fused silica slip	15	3390
(C)-Standard fused silica slip only	--	4340

Further studies were made to determine the effect of fiberglas -- a low melting glass yarn -- on strength of fused silica ware. It was found that fiberglas had a softening point between 1000° F and 1100° F, but did not melt until about 1500° F.

The following procedure was developed to remove the resin coating on the fiberglas and to help keep the fibers from concentrating in the center of the bar.

(1) The resin coating was burned off at 1100° F.

(2) The fiberglas fibers were washed in a 5 per cent solution of TSPP and then rinsed in water and dried in a 1100° F kiln.

(3) The fibers were introduced into the slip mixing in a Hobart N-50 mixer, mixing for 5 minutes in gear 1 and for 30 minutes in gear 2.

The following fiberglas--fused silica compositions were studied:

A. 8 gm 1/2-inch 863 binder/1000 ml fused silica slip

B. 8 gm 1/2-inch 845 binder/1000 ml fused silica slip

C. 8 gm F/G chopped strand 1-inch AE -863 binder/1000 ml slip

D. 100 per cent fused silica

The following table is a summary of the data obtained for firing the compositions for 2 hours at various temperatures.

TABLE III

EFFECT OF FIRING TEMPERATURE ON MODULUS OF RUPTURE OF FIBERGLAS--FUSED SILICA COMPOSITIONS

Compositions	Modulus of Rupture			
	1100° F (PSI)	1200° F (PSI)	1300° F (PSI)	1400° F (PSI)
A	358	366	309	284
B	234	271	201	203
C	204	267	181	248
D	301	248	216	204

The fibers seemed to be distributed uniformly throughout the bars.

In a further effort to increase the strength of slip-cast fused silica, phosphorous pentoxide was added to the slip. It was anticipated that this might develop a strong silica-phosphate bond.

The phosphorus pentoxide was added in the form of phosphoric acid (H_3PO_4). It was found that phosphoric acid tended to cause the slip to gel as it was being cast into test bars and resulted in the formation of a laminated cross section with severe cracking of the test bars. A mixture of 500 ml of fused silica slip and 100 ml of 85 per cent phosphoric acid was dried at 250° F, calcined at 1800° F for one hour, and the resulting cake crushed and milled into a casting slip with 30 per cent water in a one-gallon ball mill for 16 hours. This treatment was an attempt to eliminate the formation of the laminated

cross section and to prevent severe cracking, and proved to be successful. Test bars cast from this slip which were fired at 2000° F for 4 hours exhibited transverse strengths of 4028 psi and withstood the thermal shock of being quenched in water from 2000° F.

The general procedure for adding the phosphorous pentoxide to fused silica was as follows:

> Twenty per cent by volume of 85 per cent concentrated phosphoric acid was added to a fused silica slip. The slip was dried and calcined at 1800° F for one hour. The resulting cake was crushed and remilled in a gallon ball mill for 16 hours. The per cent solids concentration of this slip was 71.

Preliminary firing time--temperature studies of the phosphate-treated fused silica slips indicated an increase in strength with an increase in firing time and temperature. Transverse strengths in the range of 8000 psi were obtained for specimens which were fired at 800° F for one-half hour, then raised to 1800° F for one hour. The specimens were then placed in a furnace at 2200° F and allowed to cool to 1875° F over a period of 16 hours, after which they were air quenched to room temperature. Six of eight bars thermal cracked under this treatment and exhibited a vitreous cross section.

Additions of phosphoric acid to the fused silica slips were made, and the viscosity and pH of these slips were determined. The greatest average transverse strength of 1825 psi for test bars fired at 2000° F for one hour was exhibited by the slip having a pH of 4.8.

In conjunction with the phosphoric acid additions to the fused silica slips, another technique of introducing phosphorous pentoxide to fused silica was investigated as a result of work being done on another project at Georgia

Tech. This technique was essentially the soaking of fired fused silica ware in phosphoric acid, drying and refiring the ware. Test bars, fired at 1800° F for one hour, were soaked in varying concentrations of phosphoric acid solutions, air dried and refired at 1800° F for one hour. The test bars soaked in a 34 per cent phosphoric acid solution exhibited the highest average transverse strength, which was 3823 psi. Test bars formed by this technique exhibited no shrinkage and had a cross section which appeared vitreous. The water of absorption was 3 to 4 per cent.

Slip-cast fused silica test bars were soaked in a 35.7 per cent by weight phosphoric acid solution under a 30-inch vacuum for one-half hour, and then soaked under a pressure of 40 psi for 1/2, 1, 2, and 4 hours. The test bars were then dried at room temperature overnight, dried at 230° F for 24 hours, fired from room temerpature to 600° F for one hour, then to 1800° F for one hour. The table below lists the effect of soaking time on the strength of the test bars. Maximum transverse strength was obtained for the one-hour soaking period.

TABLE IV

EFFECT OF PHOSPHORIC ACID SOAKING TIME ON STRENGTH OF FUSED SILICA WARE

Soaking Time (Hr)	Average Transverse Strength (PSI)
1/2	2801
1	2866
2	2421
4	1694

The effect of bisque firing temperature on the strength of test bars which were subsequently soaked in phosphoric acid was studied. Test specimens were bisque fired at 1000°, 1250° and 1500° F, soaked in a 45 per cent by weight phosphoric acid solution under a 28-inch vacuum for one hour and then under a pressure of 40 psi for 2 hours. The specimens were dried and refired from room temperature to 600° F for one hour and then to 1800° F for one hour. The results of this study listed in Table V indicated that a bisque firing temperature of 1500° F exhibited the highest transverse strength.

TABLE V

EFFECT OF BISQUE FIRING TEMPERATURE
ON PHOSPHORIC-ACID-SOAKED FUSED SILICA WARE

Temperature (° F)	Average Transverse Strength (PSI)
1000	2827
1250	3129
1500	4012

Slip-cast fused silica test bars were fired at 1500° F for one hour, soaked in a 45 per cent by weight phosphoric acid solution under a 28-inch vacuum for one-half hour, then soaked under atmospheric pressure for one-half hour and one hour; under 40 psi pressure for 1/2, 2, and 4 hours. The treated bars were air dried for 24 hours and dried at 230° F overnight. The bars were then placed into a cold kiln, slowly fired to 600° F, held at this temperature for one hour, fired slowly to 1800° F and held at this temperature for one hour. Standard test bars, which were not soaked with phosphoric acid but which were fired at 1500° F and 1800° F, exhibited respective average transverse

strengths of 394 and 597 psi. The phosphate-treated bars that exhibited the greatest strength were the bars that were soaked under a pressure of 40 psi for 1/2 and 4 hours. Their respective average transverse strengths were 3292 and 3406 psi. They also exhibited the lowest water absorptions which were 4.98 and 5.99 per cent.

Pyrometric Cone Equivalents (PCE) were made of slip-cast fused silica soaked in 45 per cent by weight of phosphoric acid solutions. PCE determinations were made on specimens soaked under 40 psi for 2 and 4 hours and subsequently fired to 1800° F and 2000° F. The PCE of these specimens varied from Cone 32, Cone 32-1/2 to Cone 33. These cones represent temperatures between 3092° F and 3137° F. The differences in the melting points of these samples were not significant so that any conclusions of the effect of soaking in phosphoric acid on the melting point of fused silica could be drawn. The theoretical melting point of fused silica is 3146° F or between Cone 32-1/2 and Cone 33.

From the previous phosphate studies the following standard procedure for soaking slip-cast fused silica test bars was developed:

1. Fire test bars at 1500° F for one hour and cool to room temperature.
2. Draw 28 inches vacuum on fired test bars for one-half hour, introduce phosphoric acid and allow test bars to soak in acid for one-half hour under vacuum.
3. Release vacuum and then soak test bars under 40 psi pressure for 2 hours.
4. Allow test bars to dry for 24 hours at room temperature and complete drying operation in dryer at 230° F for 15 hours.
5. Fire test bars slowly from dryer temperature to 600° F, hold for one hour; slowly fire from 600° to 1800° F and hold for one hour.

Slip-cast fused silica test bars were fired and soaked in phosphoric acid by the standard procedure. The test bars were then fired to 2200° F for one hour. Half of the bars were air-quenched and the remaining half were slowly cooled in the kiln to room temperature. The air-quenched bars failed. The bars that were cooled slowly exhibited an average transverse strength of 6331 psi, a specific gravity of 2.09 and a water absorption of 2.97 per cent. X-ray diffraction analysis indicated that these test bars contained 25 to 50 per cent cristobalite. This may explain why the air-quenched bars failed, and the high strength exhibited by the test bars cooled slowly could also be due to the cristobalite prestressing the bar.

The effect of the addition of the acid oxides, chromic oxide and manganese dioxide, on the strength of fused silica was investigated. Test bars were cast from fused silica slips containing 8 per cent by weight chromic oxide or 8 per cent by weight manganese dioxide. The test bars were air dried, dried at 230° F and fired to 1800° F for one hour and to 2000° F for one hour. The results of these studies indicated no noticeable improvement of the strength of the cast fused silica ware.

Test bars cast from fused silica slip were soaked in chromic acid by the standard procedure. The test bars were given a final fire at 2000° F for one hour and 2200° F for one hour. The corresponding average transverse strengths were 1349 psi and 1509 psi.

Thermal expansion determinations were made on cast fused silica specimens soaked in a phosphoric acid solution using the standard soaking method previously described. The coefficient of thermal expansion of the phosphoric acid-soaked cast fused silica was found to be 1.041×10^{-6} in./in./° C from

room temperature to 1000° C. The coefficient of thermal expansion of cast fused silica over the same temperature range is 0.5×10^{-6} in./in./° C. Thus it appears that phosphoric acid soaking tended to increase the thermal expansion of the fused silica by a factor slightly greater than 2. X-ray diffraction traces were made of the phosphoric acid-soaked slip-cast fused silica and the specimens indicated 4 per cent cristobalite.

B. Dry Pressing of Fused Silica Grain

Dry pressing of fused silica grain was investigated as a possible method for forming nose cones. Dry pressing is usually accomplished by compacting with pressure a slightly wetted, 5- to 15-per-cent, material in a suitable mold. The wetting constituent can act as a lubricant or binder or both. The lubricant-binder is usually removed from the compacted material during the drying and firing operation.

Compacting dies for forming 4HT burner test plates and 164HT burner nose cone tip configurations were constructed. These two dies with their pressed compacts can be seen in Figures 5 and 6. Both the 4HT and 164HT burners are rocket motor test facilities at Redstone for testing ablation rates of materials.

Colloidal silica, core oil, Carbowax, and stearic acid were used as lubricant-binders in pressing the 4HT burner test plates. The grain size of the monofractions of fused silica used for these preliminary dry-pressing investigations were -30+100 mesh, -100 mesh (as received), -100+325 mesh, -325 mesh and -10 microns. The -30+100 mesh and -10 micron fused silica grain could not be satisfactorily used in compacting the test plates. Thus, the monofractions of -100 mesh (as received), -100+325 mesh and -325 mesh were compacted into 4HT burner test plates using 750 psi and Ludox LS colloidal silica as the lubricant-binder in increments of 5, 10, and 15 per cent on the dry weight

basis. The test plates were dried at room temperature and at 230° F and fired at 1800° F for one hour. Lamination cracks were observed in the fired test plates. The compacting pressure was reduced to 375 psi in an attempt to eliminate the laminate cracks, but the laminate cracks were still evident in these fired test plates.

A series of test plates were compacted using No. 6000 Carbowax as a binder-lubricant. The grain size of the fused silica and the binder additions were the same as those mentioned above; however, the compacting pressure was 750 psi. The Carbowax was liquified by heat and mixed with the fused silica. The mix was heated and pressed hot. The test plates were fired to 1800° F to burn out the Carbowax. No laminate cracks were evident; however, the fired test plates were very weak since no high temperature binder such as colloidal silica was used.

Lubricant-binder mixes of No. 4000 Carbowax and Ludox LS colloidal silica were made to take advantage of the lubricating qualities of the Carbowax and the fired bonding properties of the colloidal silica. The components of the lubricant-binder were varied from 5 to 10 per cent for the colloidal silica and from 5 to 20 per cent for the No. 4000 Carbowax. This lubricant-binder tended to improve the dry and fired strengths of the compacts; however, lamination cracks were still evident in the compacts.

The compacting pressure was increased from 375 psi and 750 psi to 3,000 psi in a further attempt to eliminate the formation of cracks in the fired compacts, but without success. This was true for all the monofractions studied with the exception of the -100 mesh (as received) material. Fired compacts of this material exhibited very few cracks.

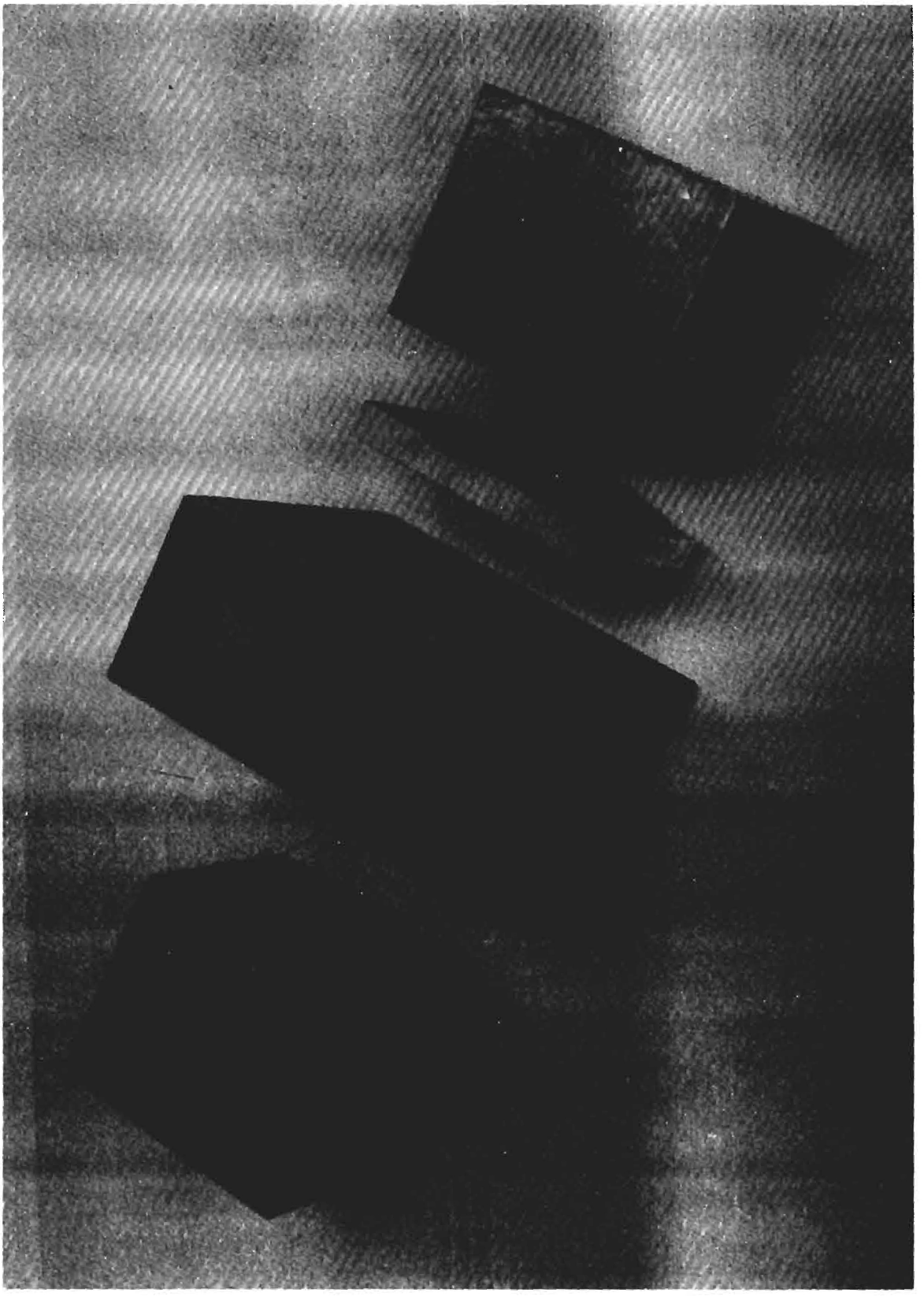


Figure 5. Die for Dry Pressing 4HT Burner Plates.

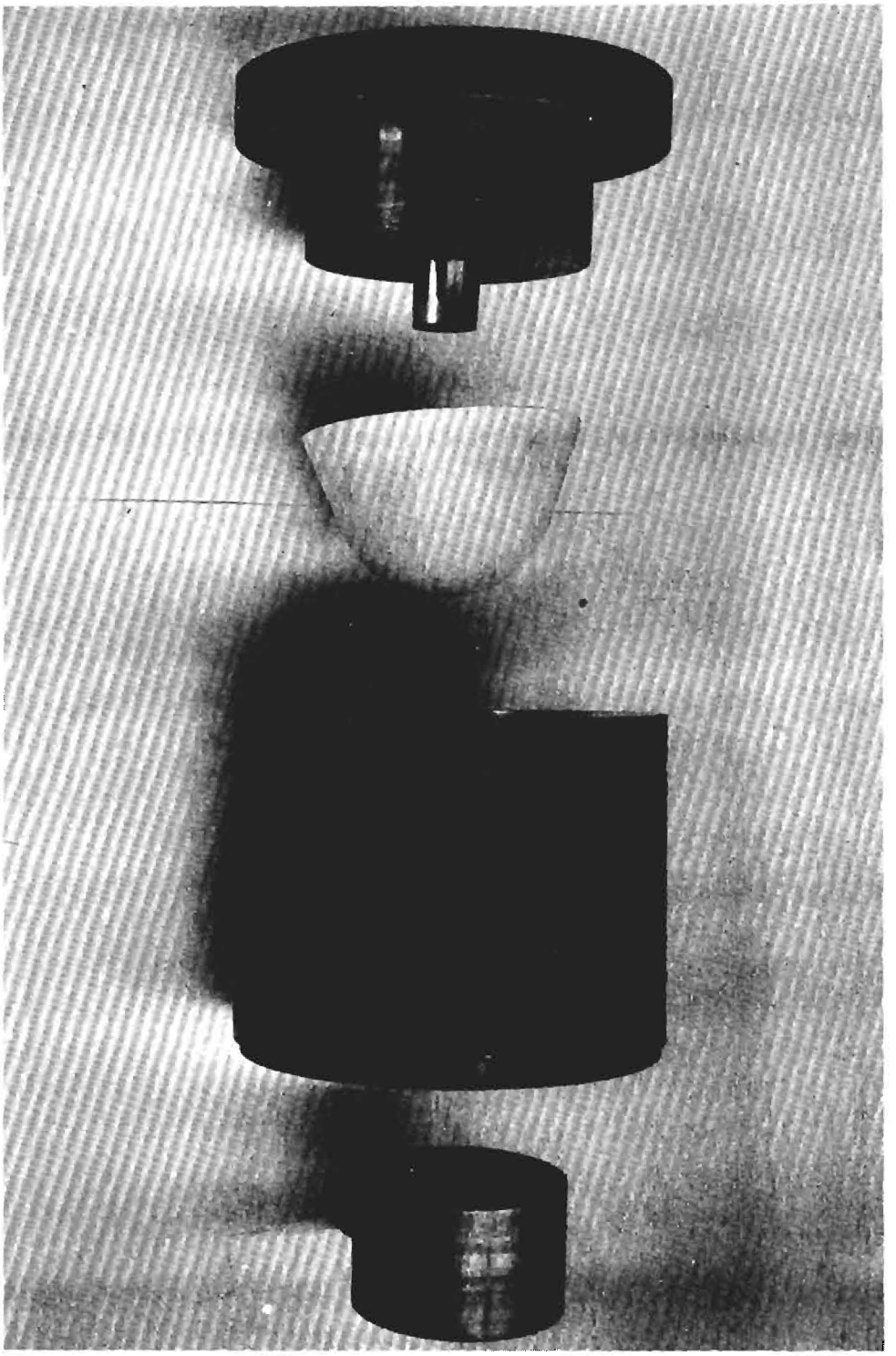


Figure 6. Die for Dry Pressing 164HT Nose Cone Tip Configuration.

In conjunction with this investigation, attempts were being made to increase the strengths of the fired compacts by soaking them in colloidal silica, then drying at 230° F and refiring at 1800° F. The strength of the compacts improved to such an extent that the soaking-refiring cycle was repeated. It was observed that the plates did not exhibit any cracks after the first soaking-refiring cycle, but became apparent after the second and third soaking-refiring cycle. The development of these cracks of course weakened the fired compacts considerably. It was considered that the development of these particular cracks was probably due to the gelling of the colloidal silica. That is, as the concentration of colloidal silica suspended in water increases, its tendency to form a gel increases and this gel has a large volume shrinkage when dehydrated. If this gel was localized at the surface of the compact it would cause the formation of cracks upon its dehydration by placing the surface of the compacts in tension so that the surface would tend to pull away from the weakened subsurface. It is not known whether this gelling occurs during soaking or drying of the dry-pressed burner plates.

If the colloidal silica could be gelled in place by some additive, such as ammonium chloride or hydrochloric acid, the shrinking of the silica gel upon subsequent dehydration would place the entire body under compression, which should increase both its transverse and tensile strengths. Thus, it was felt that gelling studies should be made in an effort to improve the strengths of both cast and dry-pressed bodies made with the fused amorphous silica grain.

The preliminary work was devoted to determining the gelling time of Ludox LS, AS, SM. and HS colloidal silica using hydrochloric acid as the gelling agent. The hydrochloric acid gelling indicated that all of the Ludox colloidal silicas could be gelled in 8 to 12 hours by adjusting their pH to 6.0 ± 0.2.

Dry-pressed test specimens were soaked in the colloidal silicas whose pH was adjusted to 6.0 with hydrochloric acid. The specimens were kept in these solutions until complete gelling had taken place, then dried at 230° F and fired at 1800° F. The test specimens soaked in hydrochloric acid-treated Ludox LS colloidal silica exhibited the highest transverse strength, 1345 psi. By comparison, a similar test specimen that was not soaked exhibited a transverse strength of 181 psi. This gelling treatment represents a sixfold increase in transverse strength.

Particle size studies of the fused silica grains were made in an effort to determine particle size distributions which could be easily dry pressed into faultless compacts. Synthetic particle size distributions were prepared by mixing three monofractions in varying proportions. The proportions were varied by 10 per cent increments. The particle size of the monofractions used were -30+100 mesh, -100+325 mesh and -325 mesh. The lubricant-binder used was Ludox LS colloidal silica and it was added to the mix in a ratio of 1 ml to 10 gm of dry material. Burner test plates were compacted from these mixes using a pressure of 3,000 psi. (The plates were fired at 1800° F for one hour, then soaked in Ludox LS colloidal silica. The colloidal silica was gelled in place using 3 ml concentrated hydrochloric acid per liter of colloidal silica, and finally refiring plates at 1800° F for one hour.)

Figure 7 is a triaxial plot of the effect of particle size on the strength of dry-pressed fused silica grain. The shaded areas are the highest transverse strengths obtained by the corresponding mixes of the three monofractions studied. From the plot it can be seen that a mix of 60 per cent -325 mesh, 40 per cent -30+100 mesh fused silica grain exhibited the highest average transverse strength, which was 1094 psi. In general, the transverse strengths

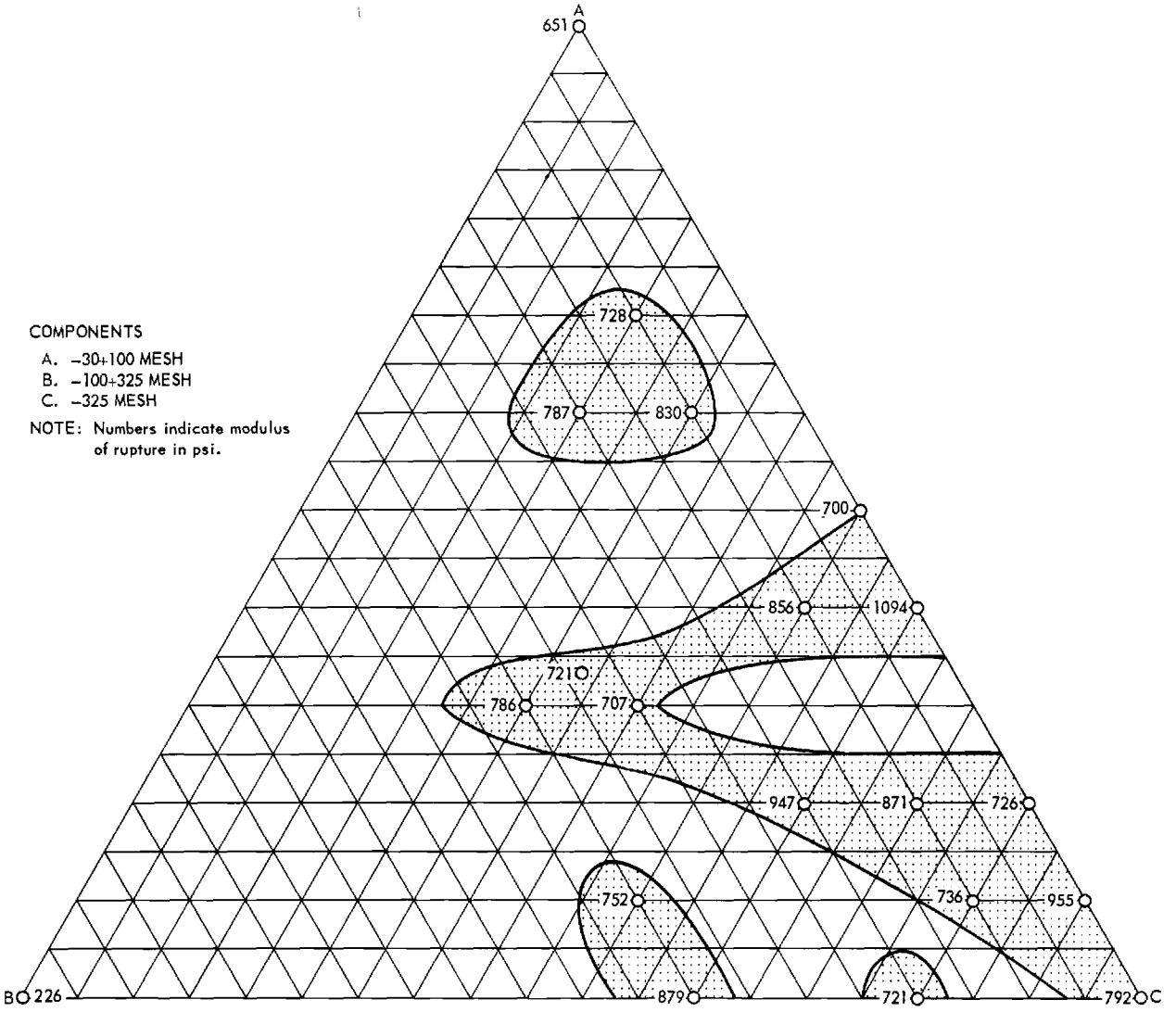


Figure 7. Effect of Particle Size on the Strength of Dry-Pressed Fused Silica Grain.

of these studies were inconsistent within a specified point studied, i.e., out of eight bars broken for this point the lowest value was 833 psi and the highest value was 1605 psi. These inconsistencies were thought to be caused by the following forming variables:

1. Compacting Pressure: As a general rule various particle sizes require various compacting pressures; however, these pressures can at times overlap. Since this study included several controlled variables, the compacting pressure was held constant at 3000 psi as an expediency.

2. Lubricant-Binder: The same applies for the lubricant-binder as in the compacting pressure of Item 1.

Several points of the particle size studies were selected and new burner test plates were made of these points. The compacting pressure was varied from 1000 to 3000 psi. The lubricant-binder addition was varied from 5 to 20 per cent. Drying and and firing of the plates were closely controlled. The transverse strengths in this additional study were still inconsistent within a specified point studied; however, it was observed that the transverse strengths increased as the compacting pressure and lubricant-binder addition were increased.

A solid nose cone tip was compacted with the die shown in Figure 6 using 6000 psi. The dry-press mix for this compact was made with -100 mesh fused amorphous silica (as received) and using 10 per cent No. 4000 Carbowax, 10 per cent Ludox LS colloidal silica as lubricant-binders. The nose cone was dried at room temperature, dewaxed at 300° F and then 500° F and fired to 1800° F and held for one hour. Its strength was low and it tended to frangible.

An attempt to improve the transverse strength of the dry-pressed fused

amorphous silica grain by resin impregnation was investigated. Burner test plates were formed of -325 mesh silica, using 25 per cent Ludox LS colloidal silica as a binder-lubricant. The plates were compacted using 3000 psi pressure. The test plates were dried at 230° F and fired at 1800° F for one hour. The plates were impregnated with Shell Epon 1310 and CTL-91-LD resins by vacuum-pressure methods. The Shell Epon 1310 resin increased the transverse strength of the dry-pressed burner plate by 5000 psi, whereas the CTL-91-LD resin improved the strength by 2500 psi. Table VI summarizes this study.

At this point the dry-pressing investigations were abandoned in preference to the slip casting of fused silica, since this fabrication technique had been developed to such an extent that nose cone hardware could be fabricated with relative ease and little expense.

C. Fabrication of Large Nose Cones

At the termination of the first year's work on this project, it became evident that considerable progress had been made in the development of a suitable slip-casting material. It was therefore felt that some effort should be directed immediately toward the fabrication of larger and more intricate shapes.

At the suggestion that fused silica represented a promising material for the construction of radomes, a radome shape was made from aluminum bar stock and a plaster mold was cast of this shape. Figure 8 shows the mandrel and a slip-cast fused silica radome. This radome stands approximately 13 inches tall with a 6 inch diameter base. Some of the early compositions containing clay as a binder were used to fabricate such radomes. Difficulty was encountered in obtaining a crack-free casting in the straight section at the base of the

TABLE VI

EFFECT OF RESIN IMPREGNATION ON
THE STRENGTH OF DRY-PRESSED FUSED SILICA GRAIN

Plate No.	Grain Size (Mesh)	Pressing Binder Ml Ludox/ 100 Gm SiO_2	Compact Pressure (PSI)	Modulus of Rupture (PSI)		
				Epon 1310	91-LD	Before Soak
162	-30+100	15	48,000	3,000		319
150	-100+325	10	48,000		2,230	145
147	-100+325	15	48,000	3,070		171
146	-100+325	20	48,000		2,760	154
164	-325	15	32,000		3,000	244
140	-325	20	48,000	2,300		390
151A	-325	25	48,000	5,260		253
151B	-325	25	48,000		2,770	253

radome. This difficulty was overcome by an adjustment in particle size of the fused silica and the type of clay used. The experience thus gained led to the desire for early attempts at casting still larger shapes. It was felt that, should similar difficulties lie in the scaled-up shapes, we should be aware of them as soon as possible. At the suggestion of Redstone Arsenal, a nose cone design was selected which was an extended projection of the nose cone tips previously fabricated and tested on the 164HT burner. This tip was extended to provide a nose cone with an overall height of 25 inches and a base 19 inches in diameter. The cone section terminated approximately 22 inches from the tip, thus providing a 3-inch straight cylindrical section as the base.

Figure 9 shows a plaster nose cone machined to the desired dimensions. This shape was fabricated by casting a plaster cylinder about a suitable reinforcing device and subsequently machining the cured plaster. The reinforcing device and the sheet metal shell used to contain the plaster are shown in Figure 10. In order to cast a large plaster mold about the nose cone model shown in Figure 9 the device shown in Figures 11 and 12 was constructed. This device consisted of a metal hoop around which was wrapped a sheet metal band. Suitable axles welded to the hoop provided support. The sheet metal band, when secured to a base plate, served to contain the poured plaster. After the plaster had set, the metal band was removed. The resulting mold is shown in Figure 13. This mold was mounted on the dolly, shown in Figure 11, and was rotated to a vertical position, or inverted, to provide the cavity into which the fused silica slip was poured. After the slip had remained in the mold long enough to provide the desired nose cone thickness, it was then poured from the mold simply by rotating the mold itself. The mold was then brought back to the filling position until the nose cone had set up, after which the nose cone was removed by again inverting the mold. Approximately 24 hours were required for this entire operation. The nose cone was then dried and subsequently fired to 2000° F.

In order to provide a means whereby this nose cone might be evaluated with the 164HT burner, a suitable attaching device was required. Taking advantage of the experience gained in studying adhesives and cements, it was decided that a simple bracket device might be successfully cemented with Shell Epon Adhesive VI to the inside of the straight section at the nose cone base and in turn this bracket could be bolted to the desired base plate which could be mounted on the test stand of the 164HT burner. Figure 14 shows the brackets

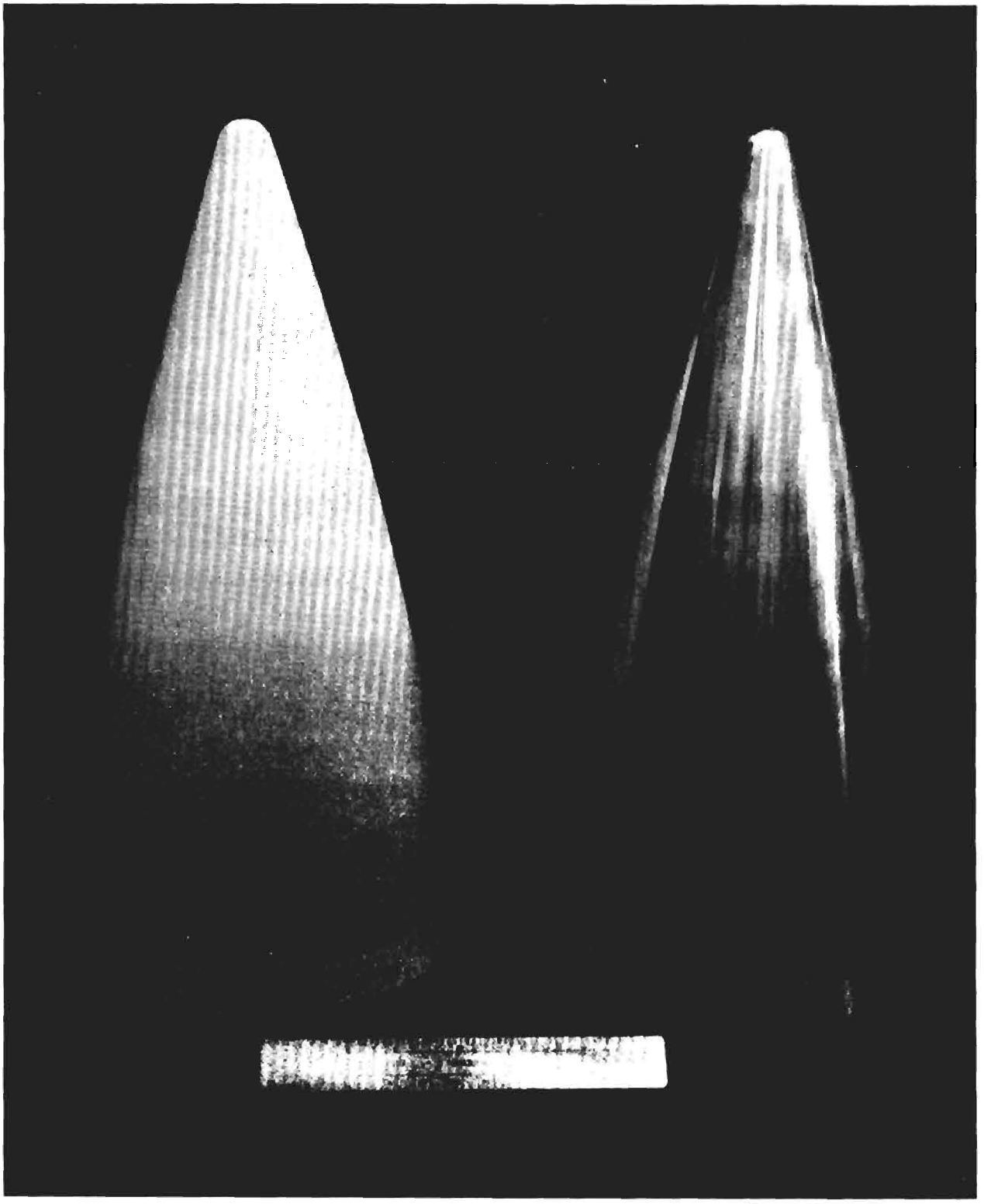


Figure 8. Slip-Cast Fused Silica Radome and Aluminum Radome Model.

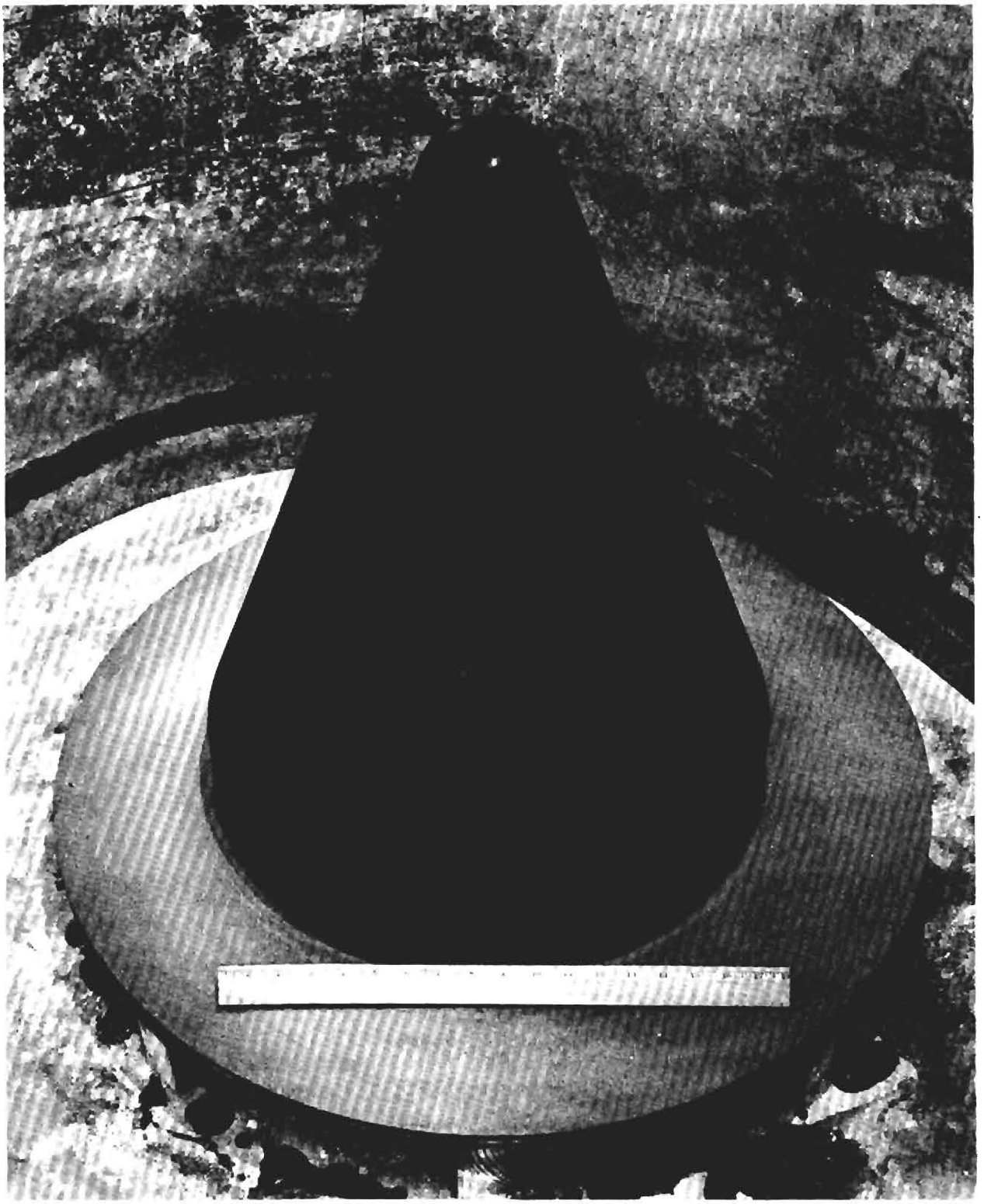


Figure 9. Plaster Model of Nose Cone Configuration. Approximately 25 Inches High.

after being cemented to the nose cone. The resulting successful testing of this nose cone with the 164HT burner proved this attaching system to be satisfactory. It should be pointed out that four such nose cones have been fabricated with relative ease and, at the present time, it is felt that there is no foreseeable size limitation in the fabrication of nose cones from fused silica. However, due to other problems such as furnaces, handling facilities and space requirements, there may be economical limitations above which size it may be desirable to fabricate nose cones in segments. A larger nose cone tip was machined from a plaster cylinder 40 inches in diameter and 22 inches in height. This cylinder has been successfully poured and weighs approximately 2,000 pounds. After the plaster was cured, the desired tip was machined and techniques very similar to those just described were used to form the desired mold in which the fused silica nose cone was slip cast. This fused silica cone tip was submitted to Redstone for evaluation. It is expected that still larger nose cones can be successfully fabricated at this laboratory.

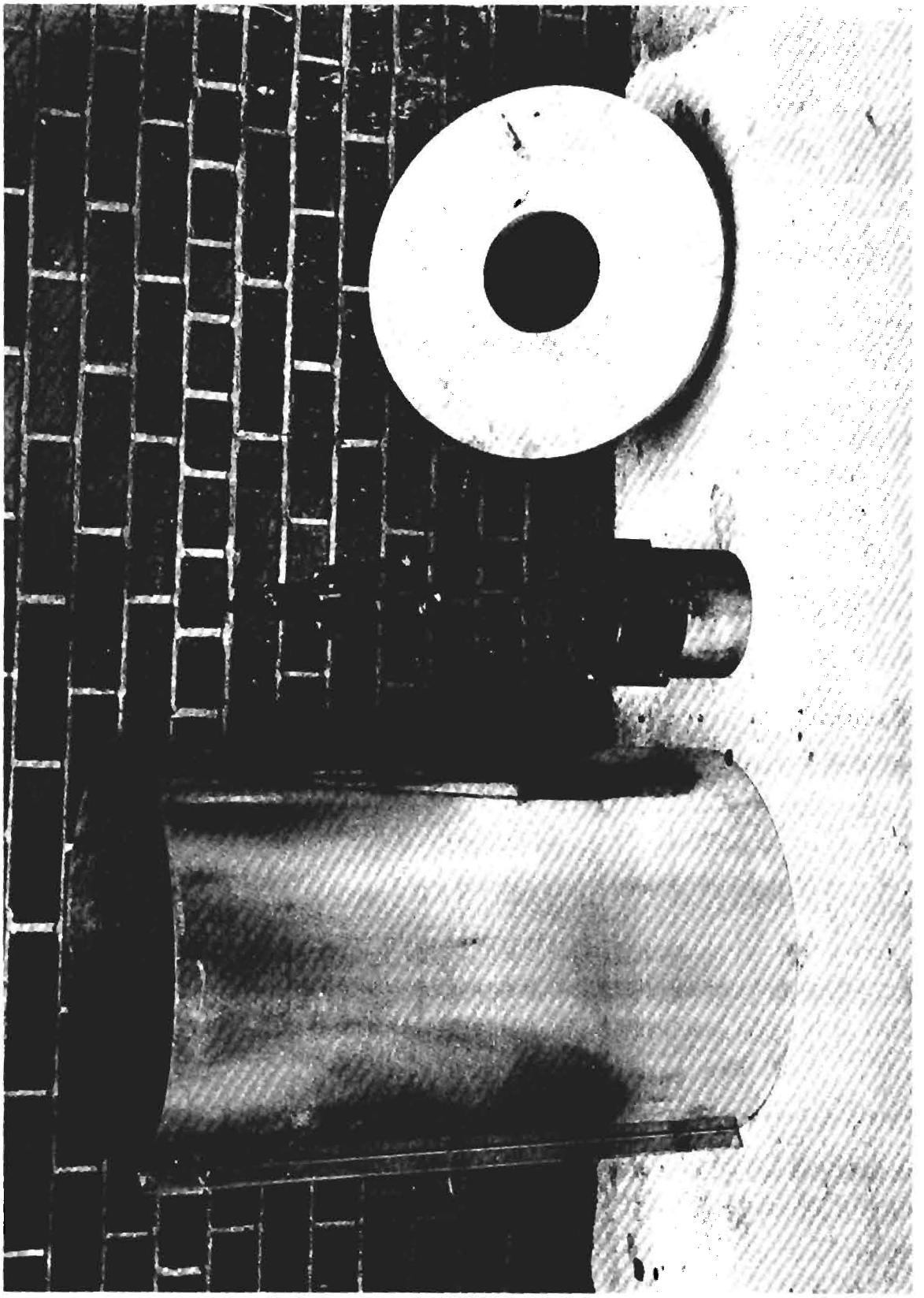


Figure 10. Reinforcing Device and Sheet Metal Frame for Casting Plaster Model of Nose Cone.

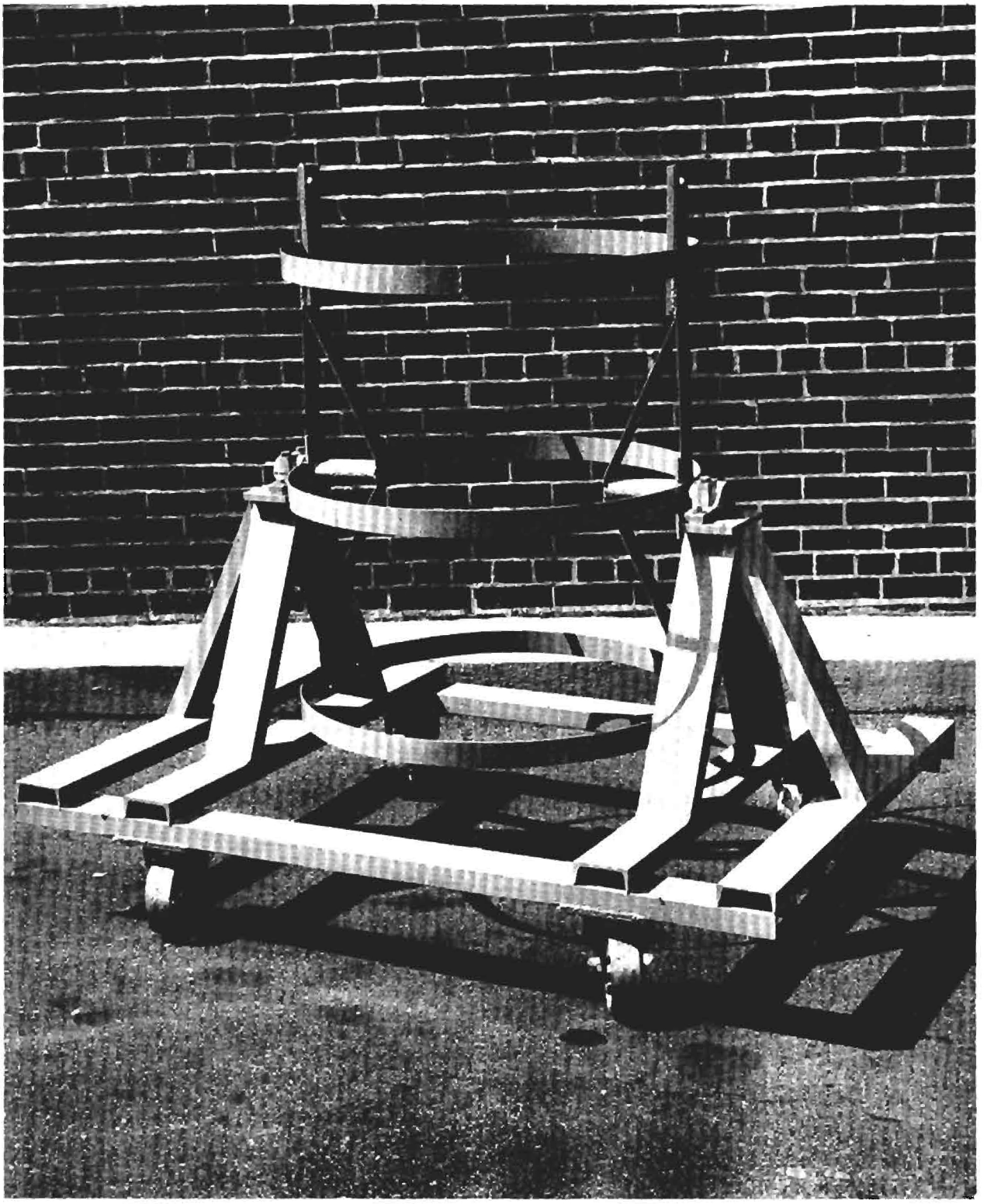


Figure 11. Nose Cone Mold Hoop Frame and Mold Support Dolly.

Figure 12. Head-on View of Nose Cone Model, Mold Frame, and Sheet Metal Band Previous to Casting Plaster Mold.

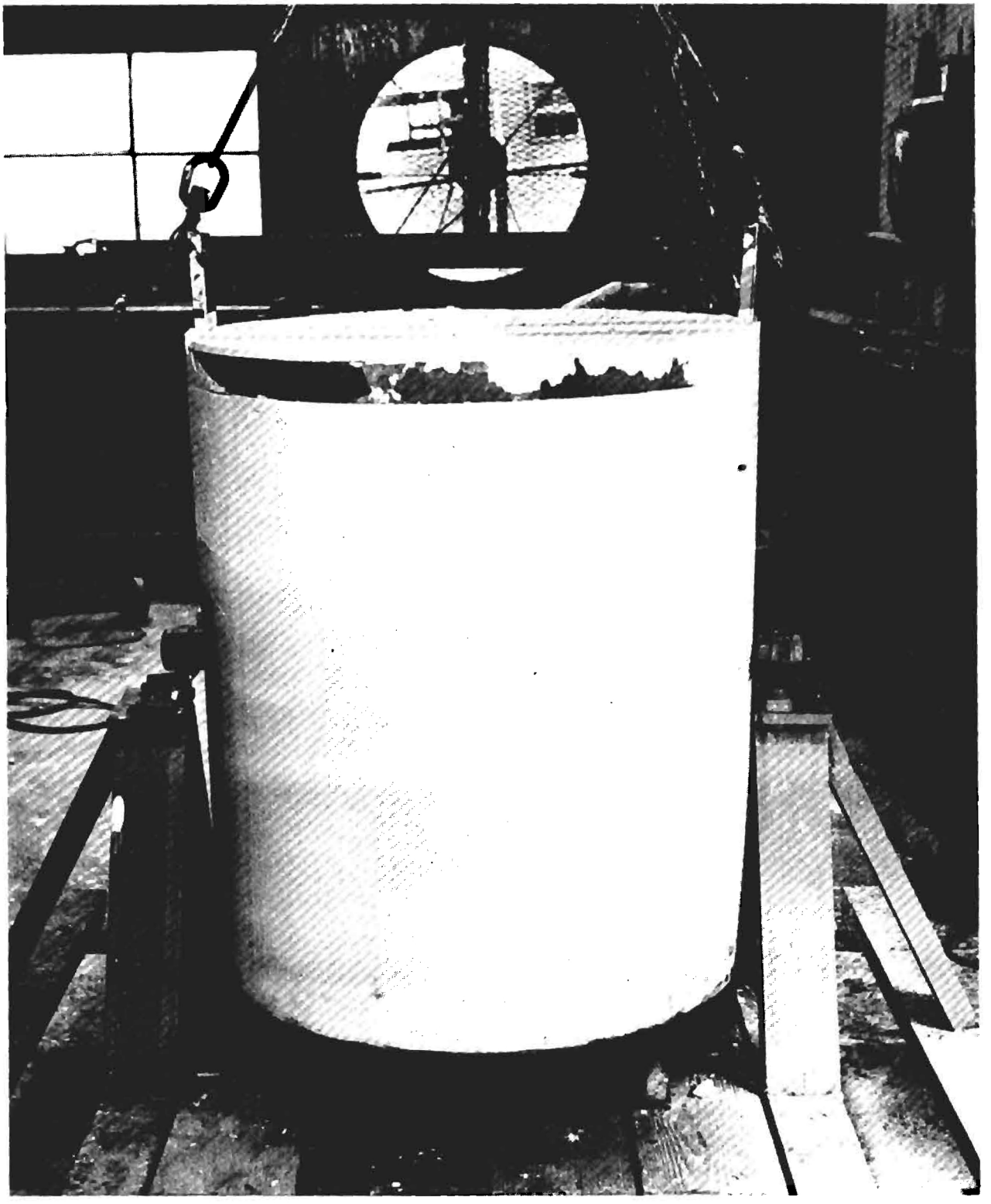


Figure 13. Plaster Nose Cone Mold After Removal of Sheet Metal Band.

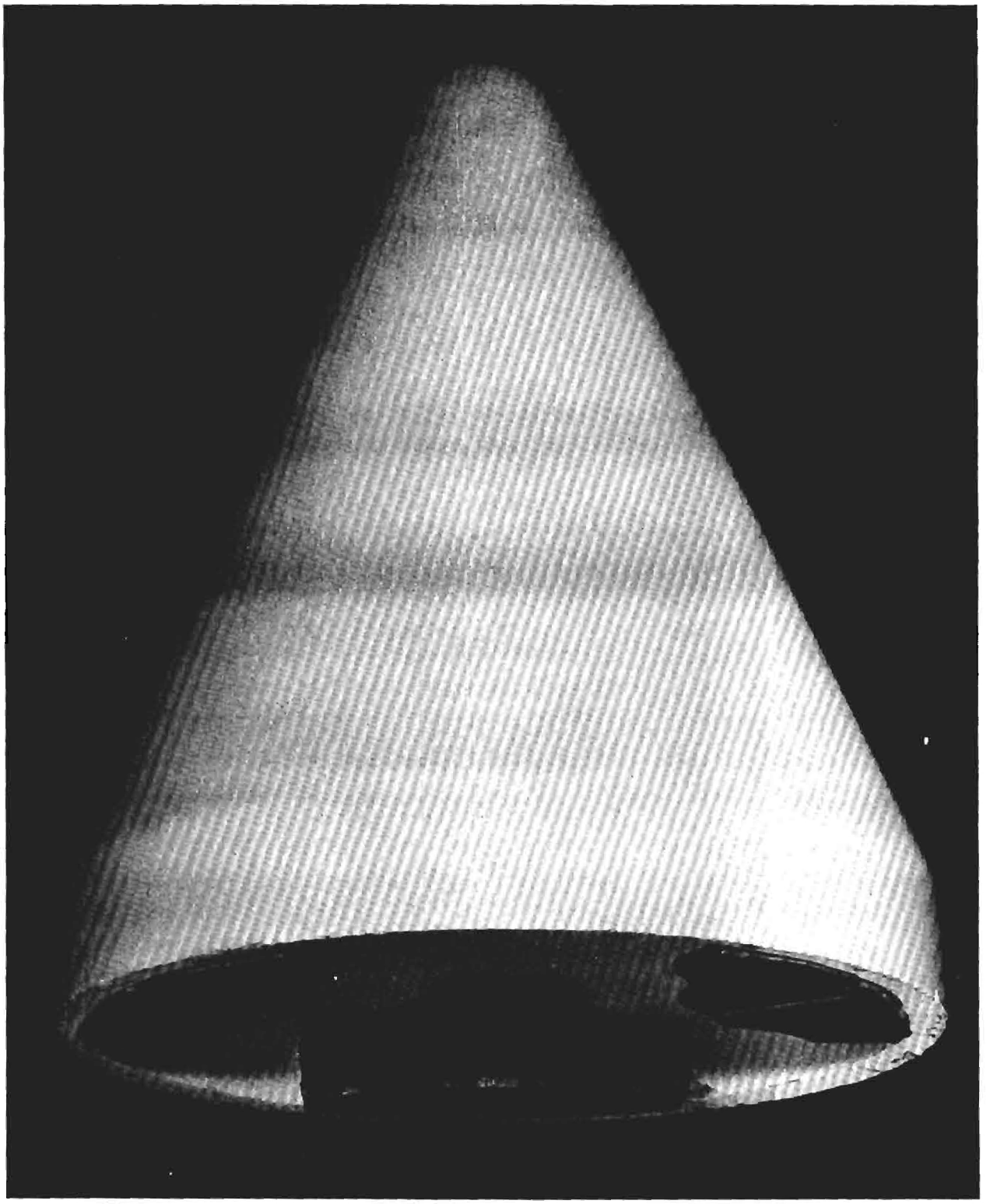


Figure 14. Fused Silica Nose Cone Showing Mounting Brackets Cemented in Place with Adhesive Resin.

D. Thermal Conductivity Apparatus

Many types of devices for measuring thermal conductivity have been constructed and used to obtain data up to a mean temperature of 1600° F. Only a few devices have been built to obtain thermal conductivities of materials above this mean temperature.

At these lower temperatures the most widely used device is a guard-ring heater. It was probably first applied by Berget[2] in 1887 in experiments on mercury and later adopted by Poensgen[2] in 1912 for thermal conductivity measurements of nonmetallic substances. In the design of the device a separate heating ring at the outer portion of a heater plate was utilized to reduce the edge losses from the main heating section.

The American Society of Testing Materials[3] has recommended the use of the guard-ring type heater in the testing of refractory materials. Work was undertaken to modify the design of this heater and its power supply so as to extend its useful temperature range to 2000° F and to incorporate it into a single piece of permanent equipment for measuring thermal conductivity of refractory type materials.

The need for a simple device which would not require cumbersome and expensive equipment to measure the thermal conductivity of various refractory-type materials prompted this work.

1. Heater Plate Construction

The main heater plates used are of the Alundum type which were originally developed by the Mellon Institute of Industrial Research. The composition of the plastic clays used are as follow:

Constituent	Percentage
Kaolin (Putnam)	30
Potter's flint	20
Feldspar (Woodcox)	35
Ball clay (Kentucky #12)	15
Total	100

Twenty per cent of the above mixture was used with 70 per cent of 38-60 mesh Alundum and 30 per cent of 180 mesh Alundum. This composition was combined with 22 per cent by weight of water to form a thick paste and cast in a wax mold.

As a matter of general interest the method of construction of the wax mold is given in detail.

An aluminum disc 10 inches in diameter and one inch thick was clamped in a lathe and recessed to a depth of 0.4375 inches and 9.250 inches in diameter. The aluminum plate was removed from the lathe and the recess was filled with a mixture of one part Gulf Petrowax A and one part paraffin wax.

After the wax had solidified the aluminum plate was centered in the chuck of the lathe and a depression cut into the wax to a depth of 0.250 inches and a diameter of 9.125 inches. The depression was increased to a total depth of 0.350 inches at the outer circumference of the 9.125-inch-diameter recess, by cutting a groove 0.094 inches wide and 0.100 inches deep at the outer circumference of the recess. A double spiral groove of five turns per inch with a width of approximately 0.060 inches was then cut into the wax to a depth of 0.100 inches.

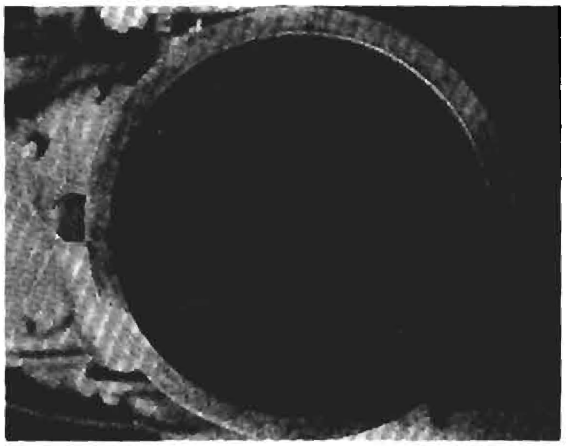
In cutting the spiral grooves the tool in Figure 15 was used. Four ribbons of wax 0.025 inch thick were cut from each groove from the outside of the plate toward the center as shown in Figure 15(B). After cutting one groove to the prescribed depth, the tool was repositioned 0.100 inch toward the center and the second spiral cut between the grooves of the first. On each cut the small end of the wax ribbon which stuck to the center of the plate was removed by hand using a small piece of wire sharpened on one end. This prevented a build-up of wax in the grooves at the center.

The wax mold was then placed on a mechanical vibrator and the mixture for the Alundum plate was poured very slowly into the mold. This allowed the grooves in the wax to fill without trapping air bubbles. The mold was filled completely, covered with a damp cloth and dried at 125° F for 18 hours. It was then placed in a high temperature drier at approximately 220° F for 8 hours.

After this drying period the Alundum plate was carefully removed from the aluminum plate and placed grooved side up on a flat surface. It was then placed in a furnace and fired to 1950° F.

The Alundum plate was then grooved for thermocouples and voltage and power leads. The back surface of the plate was ground to produce a surface as flat as possible. After all cutting operations were completed, the plate was again fired at 2540° F.

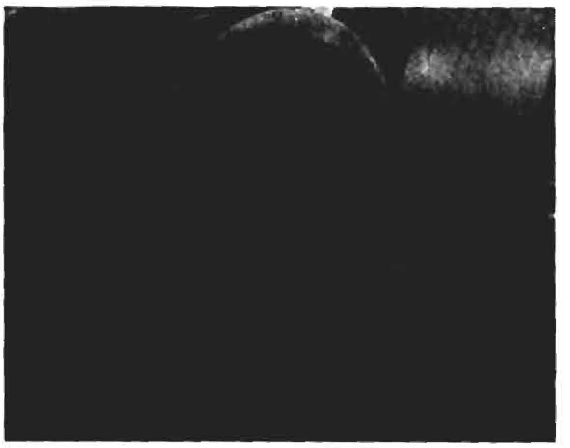
A cover plate for the main heater was made in a similar manner. A single recess 0.250 inch deep and 9.125 inch in diameter was cut into a wax-filled aluminum plate and filled with the Alundum mixture. This cover plate was cemented to the main heater after it was completely wired by Sauereisen INSA-LUTE cement. All heater plates were wound with Kanthal A-1 wire, Band S 22 gage.



A. Wax filled mold with circular groove.

B. Cutting first spiral.

C. Cutting second spiral between first spiral grooves.



D. Completed wax mold.

Figure 15. Steps in Producing Wax Mold for Heater Plates.

Two auxiliary heaters were made following the procedure already outlined with one exception. There was no need to produce two identical surfaces on these heaters as was the case with the main heater; therefore, the cover plate was not used. Instead the resistance windings were covered with Sauereisen INSA-LUTE Hi-Temp P-7 cement and after drying, ground flat. The diagram of the auxiliary heater plate circuits is shown in Figure 16. Six chromel-alumel thermocouples were used to measure temperature. Four of these were embedded in the surface of the plate along a radius. They were located so that two thermocouples were over the guard circuit and two were over the center circuit. The temperature of the low temperature surfaces was measured by placing a thermocouple in the center of the samples and insulating it from the nickel plate by a thin asbestos sheet. The maximum service temperature of this type and size thermocouple was exceeded in operation.[4] This required frequent replacement of the thermocouples.

2. Instrumentation and Equipment

The complete unit is shown in Figure 17. A sectional view of the thermal conductivity apparatus is shown in Figure 18. The rubber hoses are water supply lines to the cooling plates. A constant pressure head is maintained by a water reservoir located near the ceiling of the room. The covered tub on the rear of the control panel houses the heater plates, samples, and insulation. The volt box and potentiometer appear on the shelf below the control panel. The construction details of the cooling plates are shown in Figure 19. A schematic diagram of the cooling system is shown in Figure 20. The guard and main circuits of the main heater plate were supplied with d-c power by a compound-wound generator driven by a three-phase induction motor. The complete diagrams of these two circuits appear in Figures 21 and 22.

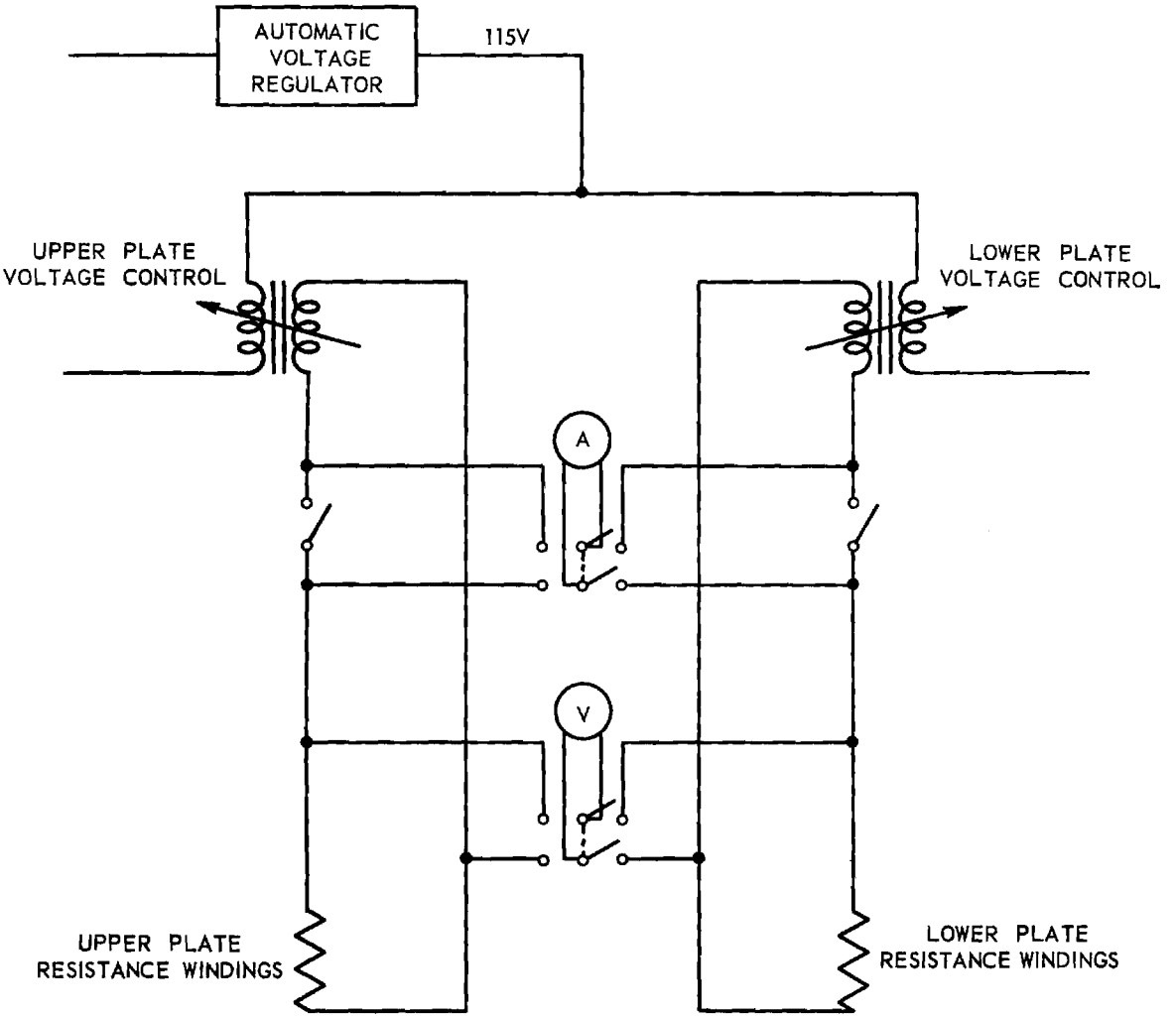


Figure 16. Auxiliary Heater Plate Circuit.

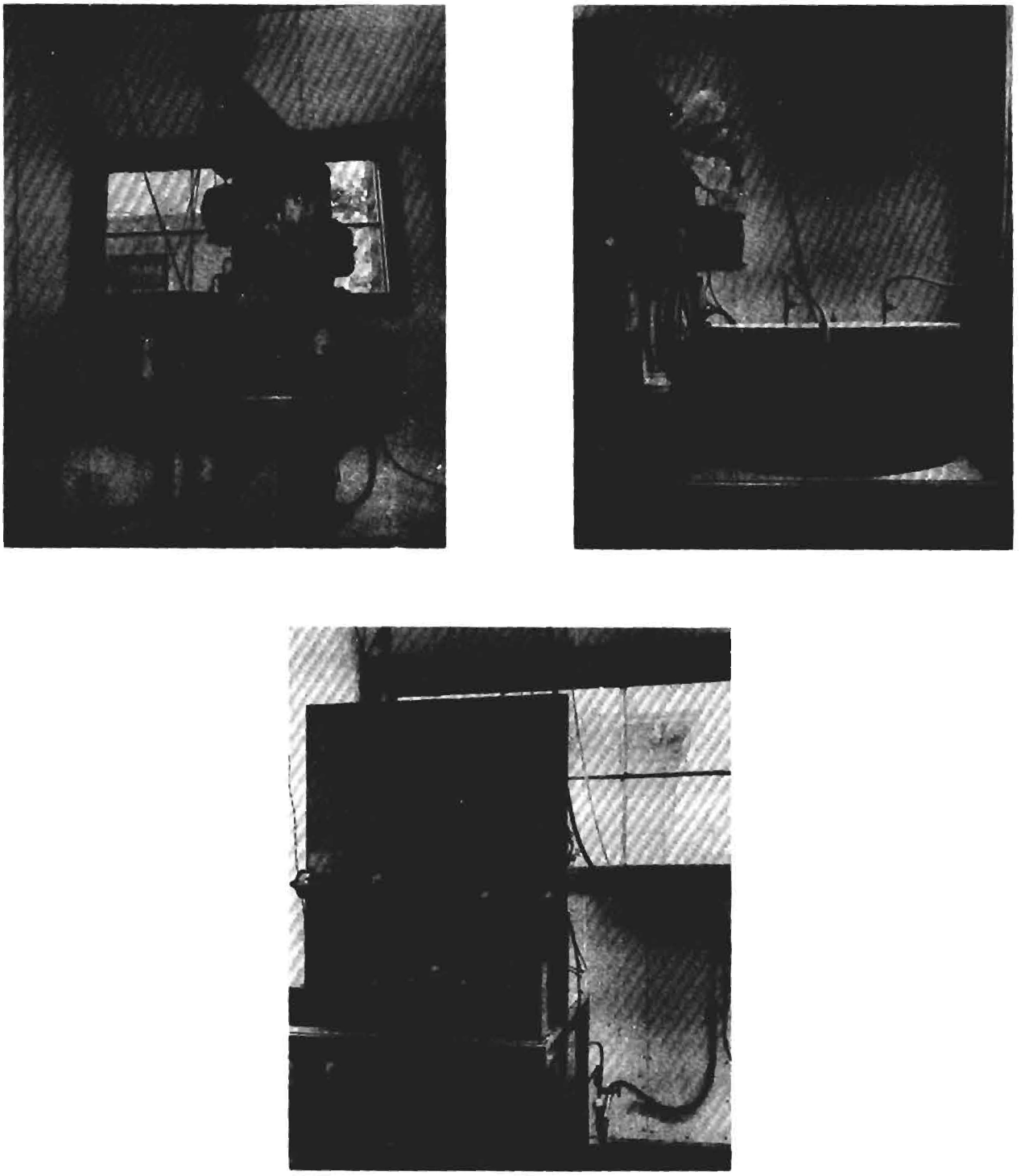


Figure 17. Three Views of Thermal Conductivity Apparatus.

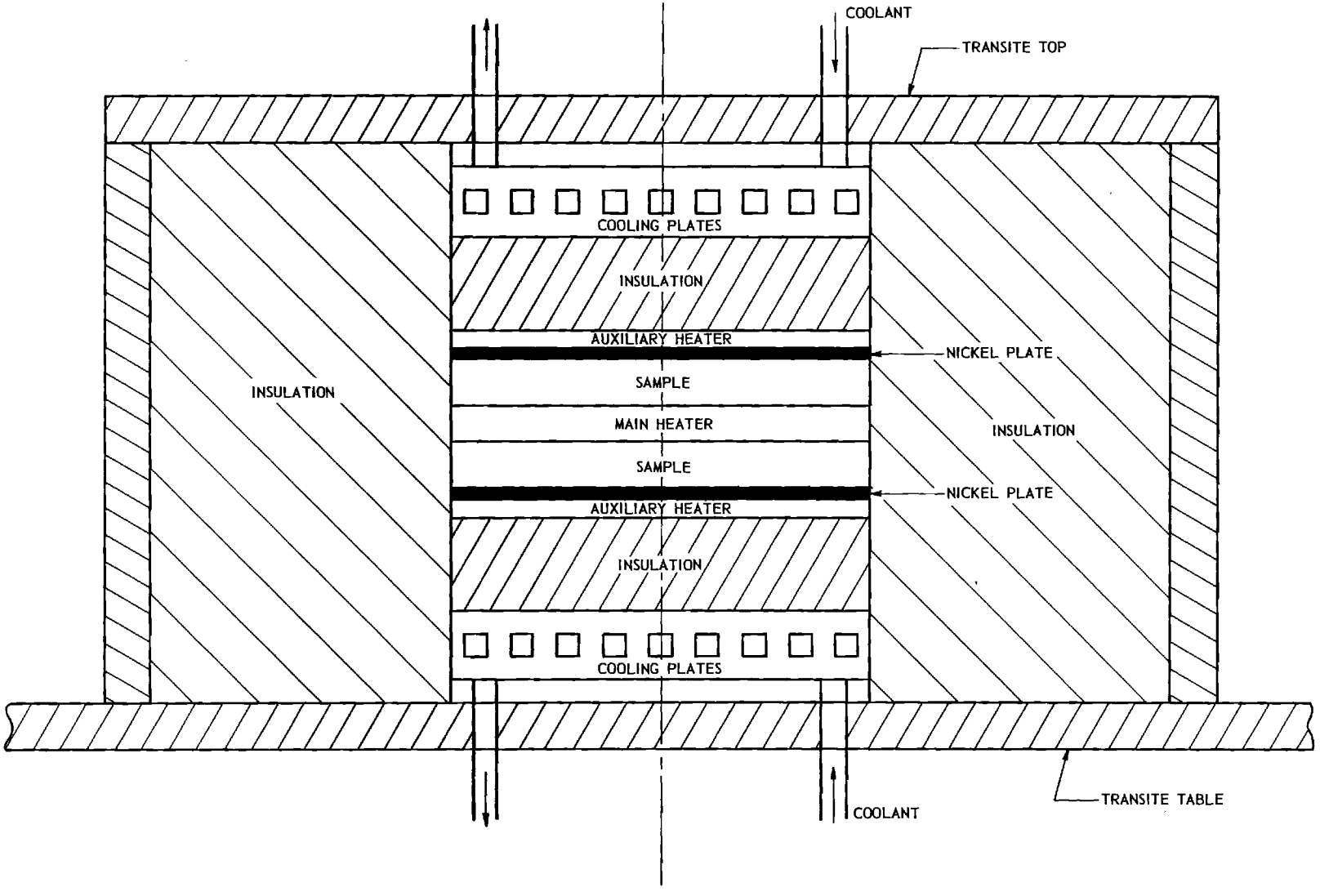


Figure 18. Sectional View of Thermal Conductivity Apparatus.

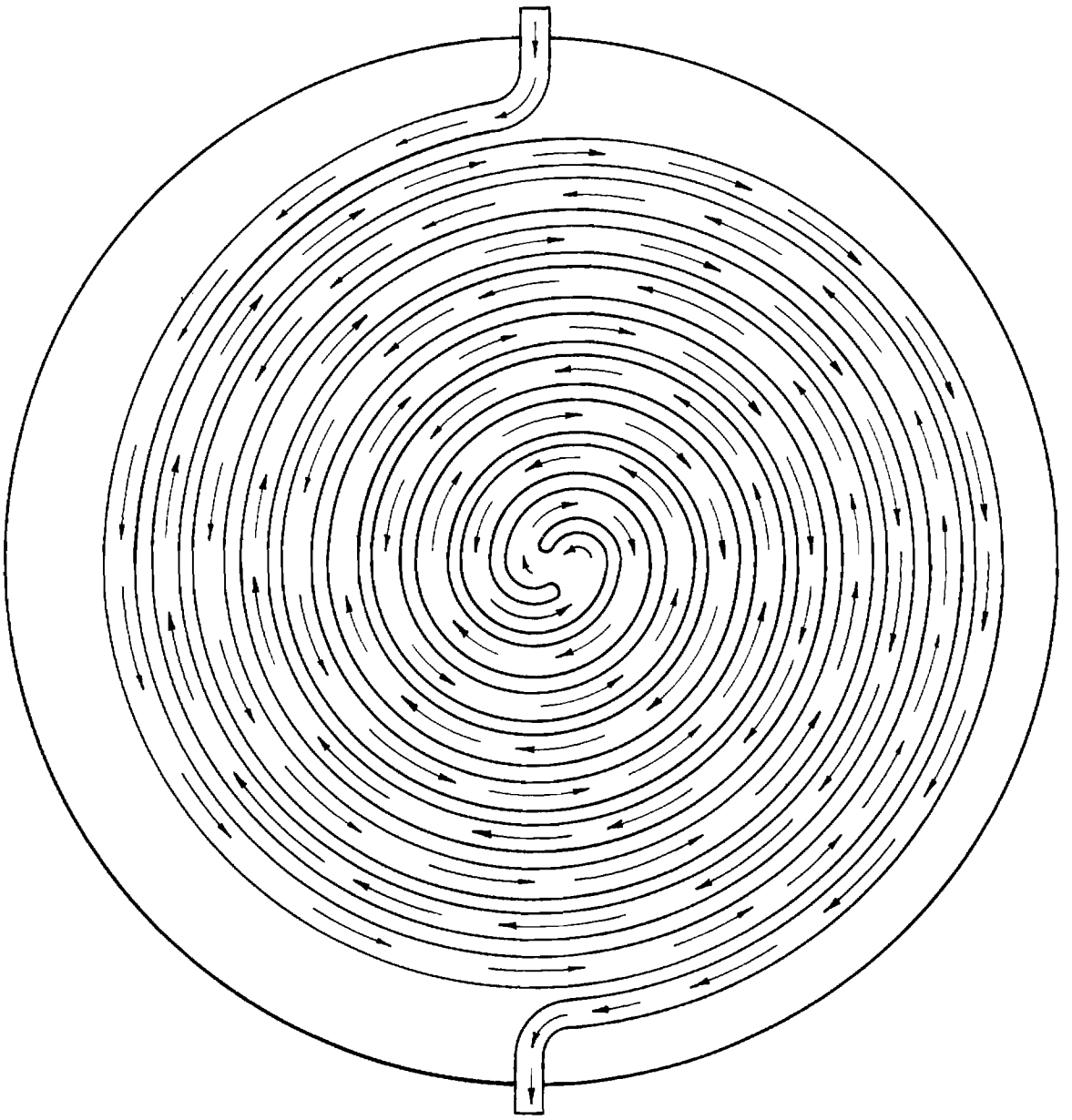


Figure 19. Top View of Cooling Plate with Cover and Gasket Removed.

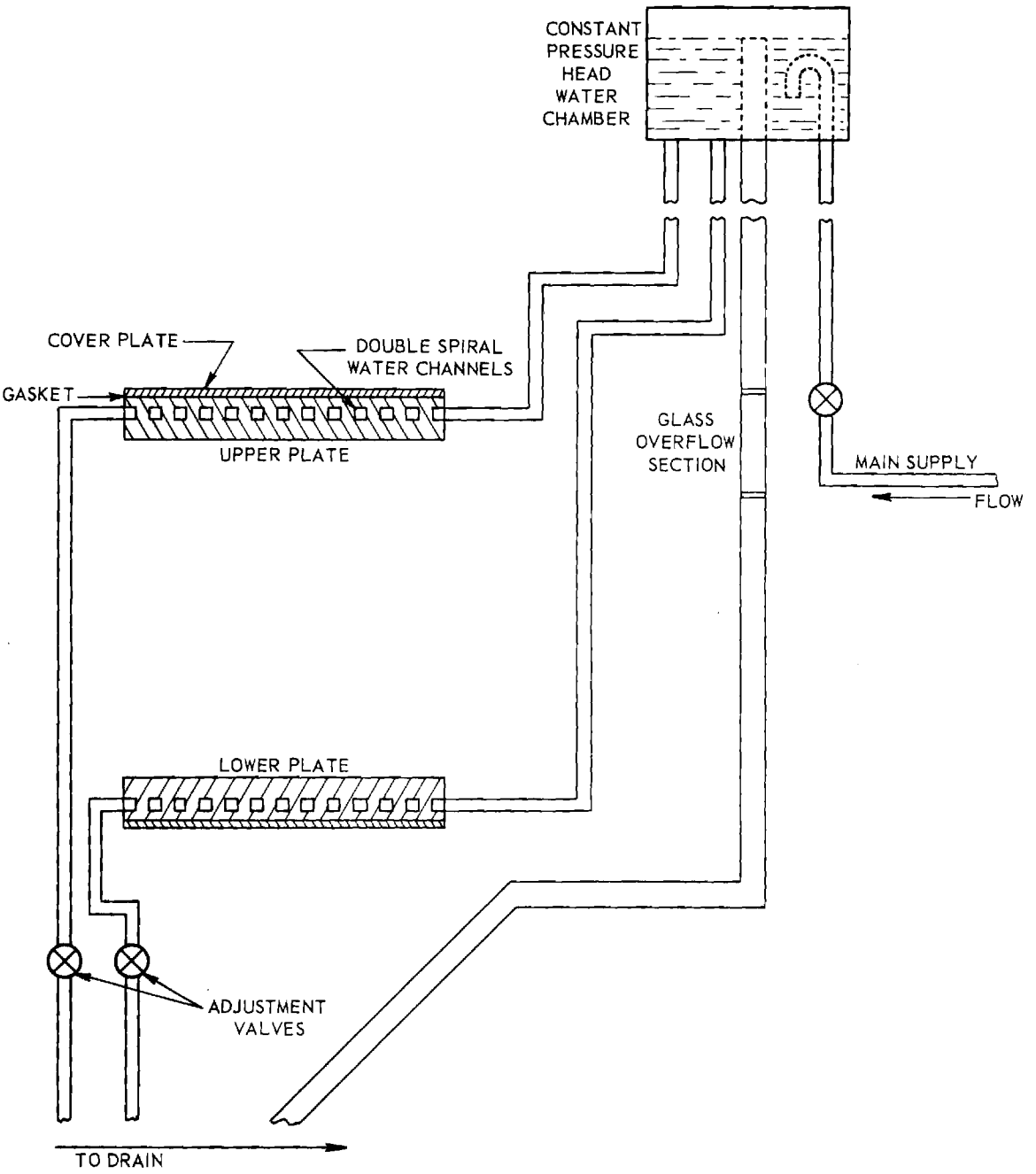


Figure 20. Schematic Diagram of Cooling System.

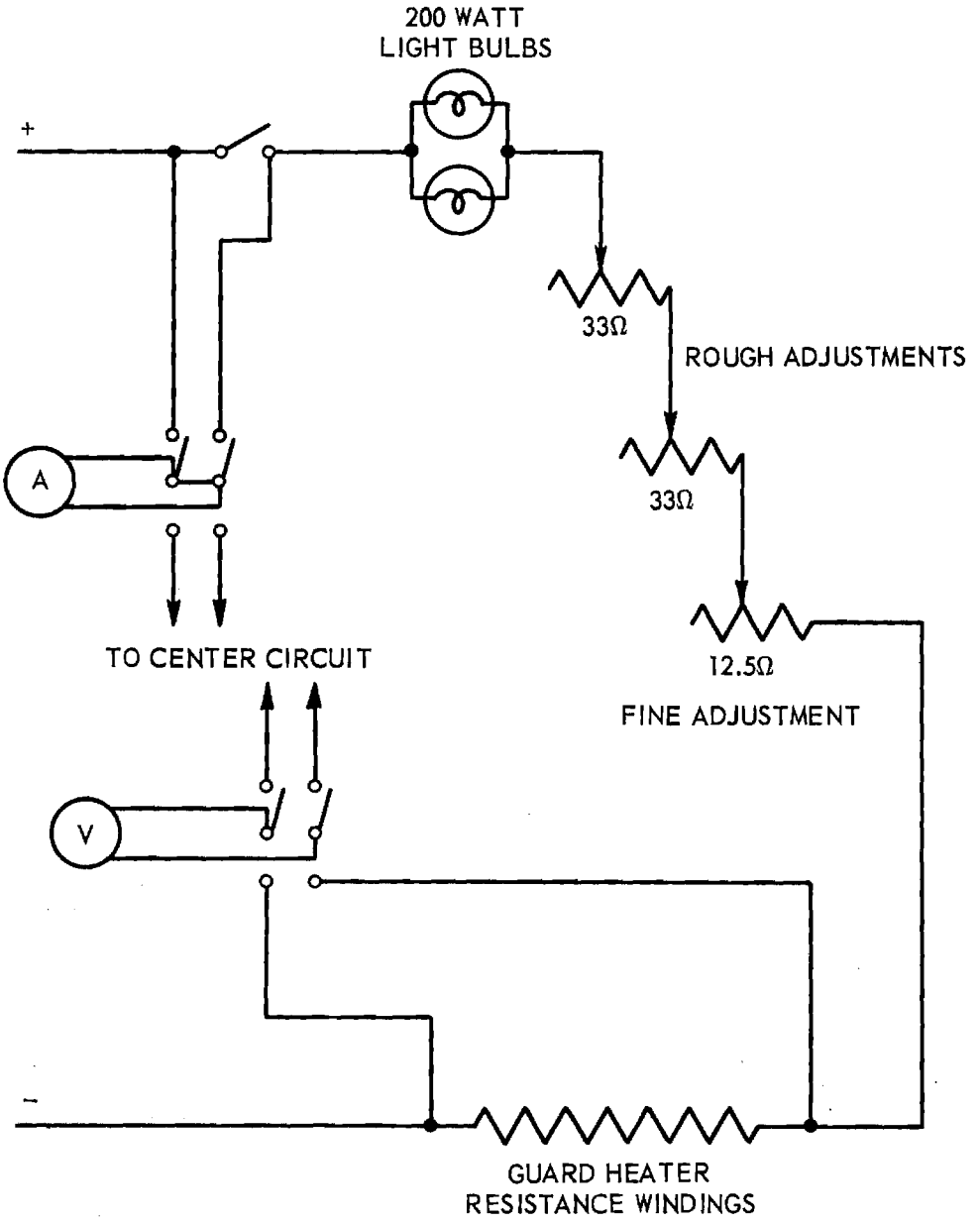


Figure 21. Center Heater Plate Guard Circuit.

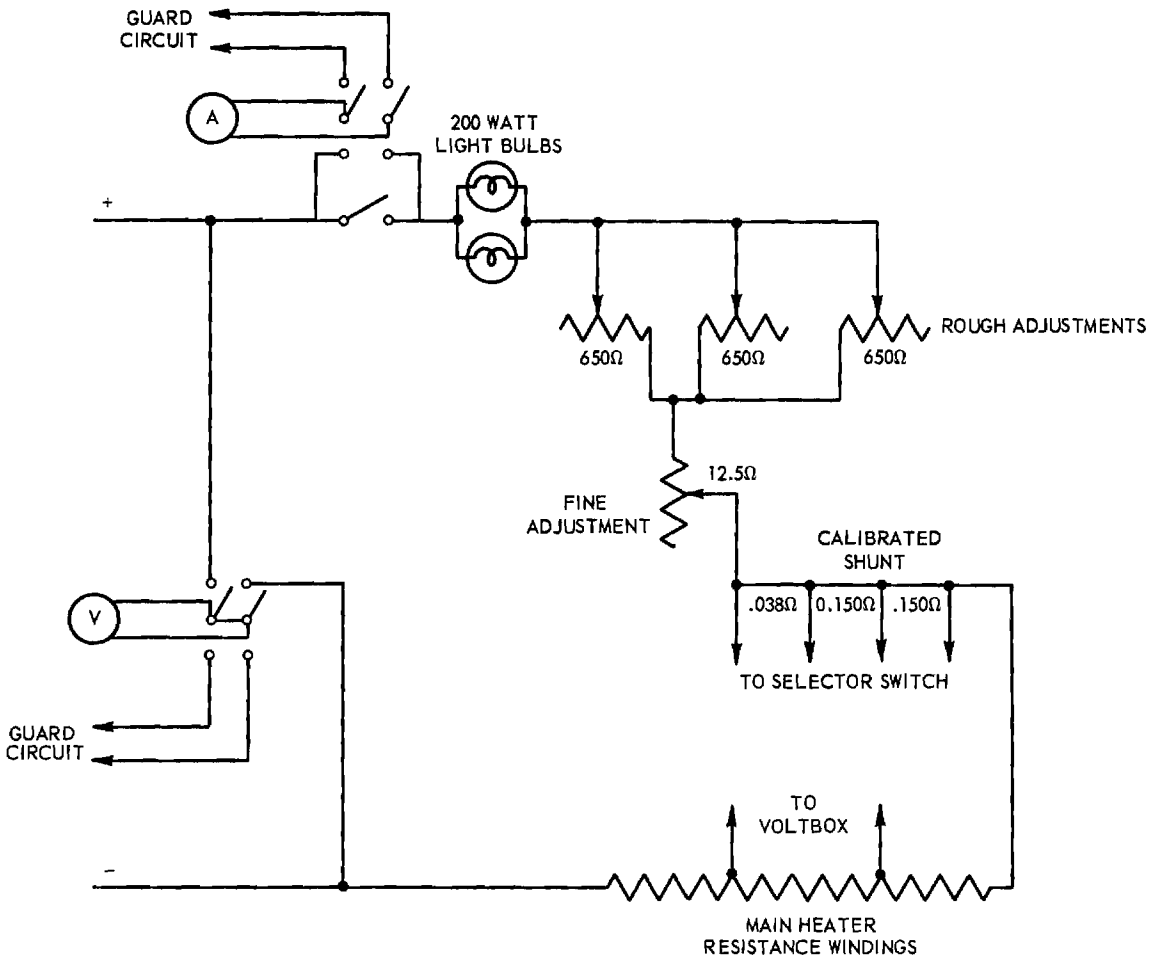


Figure 22. Center Heater Plate Center Circuit.

The guard circuit incorporated three rheostats in series with the resistance windings for control. Two of these rheostats were slide-wire resistances of 65 ohms each for rough adjustments. The third rheostat was a 12.5-ohm, circular type for fine adjustments. The maximum current in the guard ring was limited to 3.3 amperes by the ratings of the control rheostats. However, the edge losses from the heater plate were small and the maximum current required at elevated temperatures was approximately 2.0 amperes.

The main circuit utilized three slide-wire rheostats in parallel with each other for rough adjustments and a 12.5-ohm circular rheostat in series with the load for fine adjustments. The resistances of the three rheostats for rough adjustments were 650 ohms each with a maximum current rating of one-half ampere each. This limited the maximum current in the main circuit to 1.5 amperes. At the upper temperatures the current required in this circuit was approximately 1.4 amperes with a temperature drop of 51 degrees across a sample thickness of one-half inch.

A calibrated resistance shunt in series with the main circuit heater windings was used as a convenient means of measuring current accurately. This shunt was constructed of constantan wire which has a resistance-temperature coefficient of $0.000002(^\circ C)^{-1}$ at 25° C. The diagram of this shunt and its voltage measurement leads going to a selector switch are shown in Figure 22.

The voltage drop across a known area of the main heater was measured by voltage leads imbedded in the surface of the heater plate. These leads were connected through a volt-box which reduced the voltage by a known constant. This voltage was measured by a potentiometer with an accuracy of ±0.02 per cent. The voltage across the test area ranged from 5 volts at relatively low

temperatures to 35 volts at the higher temperatures. Thus, the power, EI, passing through a known area was easily determined by two settings of a selector switch, measuring at one position the voltage across a calibrated shunt and at the other, the voltage across the test area.

Considerable difficulty was experienced during initial operations of the equipment in achieving steady-state conditions because of a variation in the generator output voltage. This difficulty was removed by decreasing the resistance in the generator field so that it was operating at its most stable point and placing two 200-watt light bulbs in parallel with each other in each of the two d-c circuits. The filaments of these bulbs appeared cherry-red since only a small current was flowing in each one. Under these conditions, the filament was very sensitive to any temperature change and acted as a variable resistance in the circuit. A small change in output voltage would increase the resistance of the filament of the bulb by increasing its temperature slightly.

The two auxiliary heaters were supplied by 115 volts a-c power. Each of these plates utilized a powerstat for voltage control to the resistance windings. The two powerstats were connected in parallel to an automatic voltage regulator which maintained a constant 115-volt output.

In order to ensure that the heat flow through the test sample over the test area was perpendicular to the surfaces of the sample, nickel plates one-fourth-inch thick and 9 inches in diameter were placed between each of the auxiliary heaters and the cold surfaces of the test samples. A soft asbestos sheet one-thirty-secondth of an inch thick was placed between the nickel plate and the test sample. This allowed a thermocouple of small wire to be placed on the

test sample without completely disrupting the surface contact. The nickel plates having a high thermal conductivity ensured that at least the test area of the sample was at a constant temperature.

3. Operation of Equipment

The possibility of irreversible chemical changes occurring in the test sample required that the determination of the thermal conductivity be done in steps of increasing temperature. The requirements that steady state be achieved and that the temperatures be adjusted within very close limits at each step represented the most time-consuming part of the operation.

In starting a test run all the heaters were placed in operation at a low power setting and the valves in the water lines through the cooling plates were opened equally. During the first several hours of this initial warm-up period the temperature gradient across the guard circuit area and the main circuit area of the main heater was checked frequently to eliminate the possibility of cracking the heater plate.

Once the temperature change with time became small, minor adjustments were made in the power settings of the various heaters every few hours. These adjustments were made in order to balance the temperatures across the guard and main circuit areas of the main heater and to balance the temperatures of the cold surfaces of the two samples. When these temperatures were equal and there was no change in temperature with time, the measured values of the current, the voltage drop, and the surface temperatures were recorded.

Equalizing the temperatures of the cold surfaces of the two samples was the most difficult single adjustment. For this reason, if steady state was reached with a temperature difference of one or two degrees between the two

cold surfaces of the samples, and the temperatures between the guard and main circuit areas were equalized, then the measured heat flow was divided in proportion to the temperature drop across the samples.

4. Performance

A sample of known thermal conductivity was used to evaluate the overall performance of the equipment. This sample was a silica base solid insulation with a trade name of "Min-k 1301." The thermal conductivity values appearing in Figure 23 for this known sample were guaranteed by the manufacturer to be within 10 per cent of the actual thermal conductivity.

The results obtained with the instrument described above with the samples of known thermal conductivity are shown in Figure 23 along with the values furnished by the manufacturer. The measured values are within the limits of accuracy given by the manufacturer. However, the performance of this equipment will be largely dependent upon the surface finish of the samples. Excellent surface contact was made using the "Min-k 1301" samples. On the other hand, the surface finish of the slip-cast fused silica sample could not be produced within the tolerances specified by the ASTM Standards publications.[3]

5. Routine Calculations

The equation used to calculate the thermal conductivity is

$$k_m = C \frac{E\,I}{2\,A} \frac{T}{(t_1 - t_2)}$$

where C = dimensional constant

E = voltage across test area

I = current in the main curcuit

T = thickness of the test samples

A = area of the test section

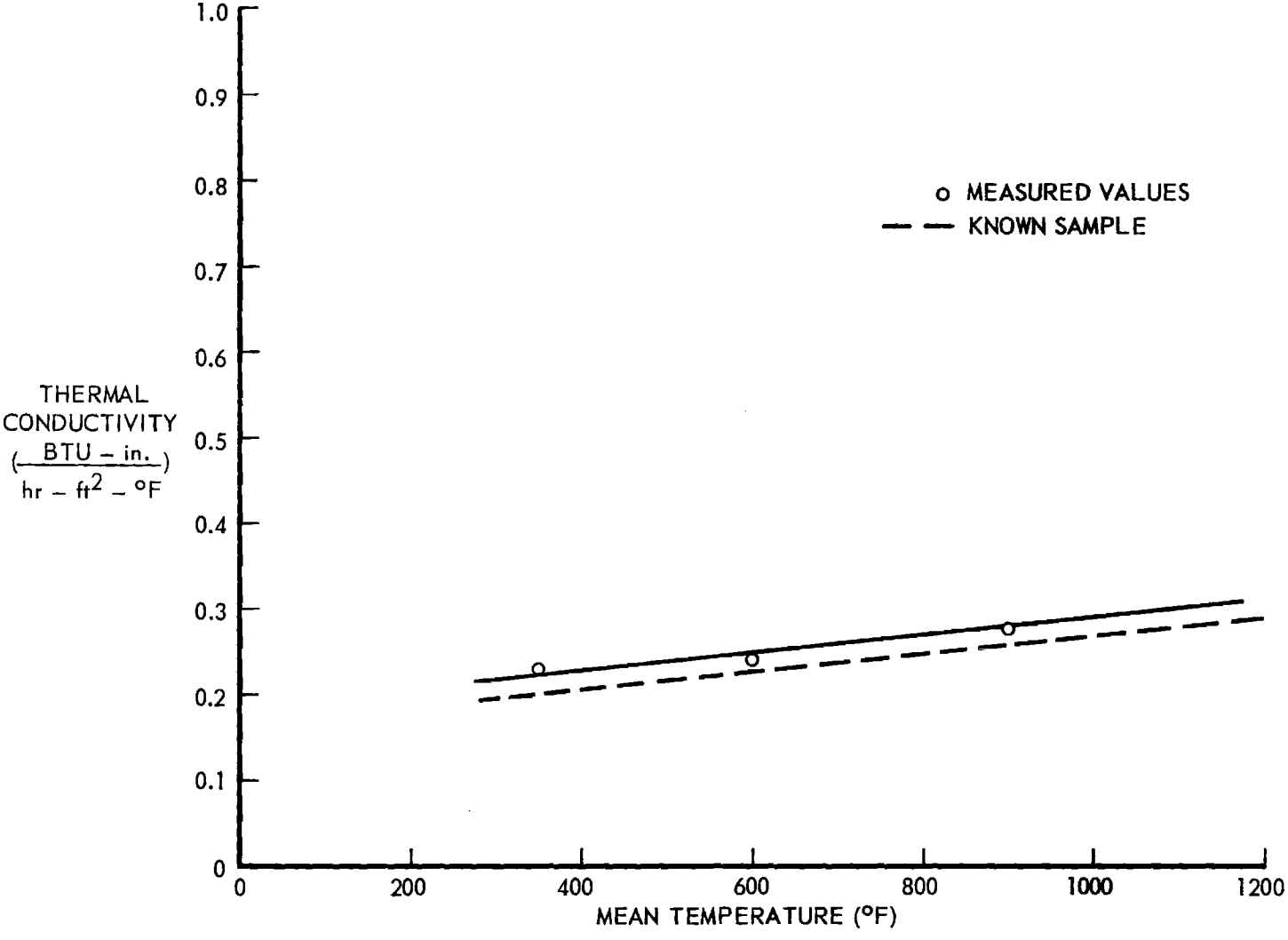


Figure 23. Comparison of Sample of Known Thermal Conductivity with Measured Values Using "Min-K 1301".

t_1 = temperature of the test area

t_2 = temperature of the cold surface of the test sample

k_m = thermal conductivity at the arithmetic mean temperature, $\frac{t_1+t_2}{2}$.

In the particular case where the temperature of the cold surfaces of the samples differed by one or two degrees the following equation was used:

$$k_m = C \frac{E\ I}{1 + \frac{t_1-t_2}{t_1-t_3}} \quad \frac{T}{A\ (t_1-t_3)}$$

where t_2 and t_3 are the temperatures of the cold surfaces.[5]

The thermal conductivity values measured using the one-quarter-inch fused silica samples are slightly different from the values determined with the one-half-inch samples. This difference is attributed to the small temperature drop across the thinner sample which resulted in a larger possible error. The two samples are shown in Figure 24. The effect of temperature on the thermal conductivity is shown in Figure 25 for the one-half-inch sample. Indications are that firing treatment previous to testing of the sample significantly affects the thermal conductivity.

The results of the performance test using "Min-k 1301" indicate that the apparatus will produce satisfactory results provided that good surface contact is made between the heaters and samples. The surfaces of the slip-cast fused silica samples could not be produced with the tolerances specified by the ASTM standards. The error that this introduces is not determined, but it can be assumed that the end result would be to lower the measured values of thermal conductivity.

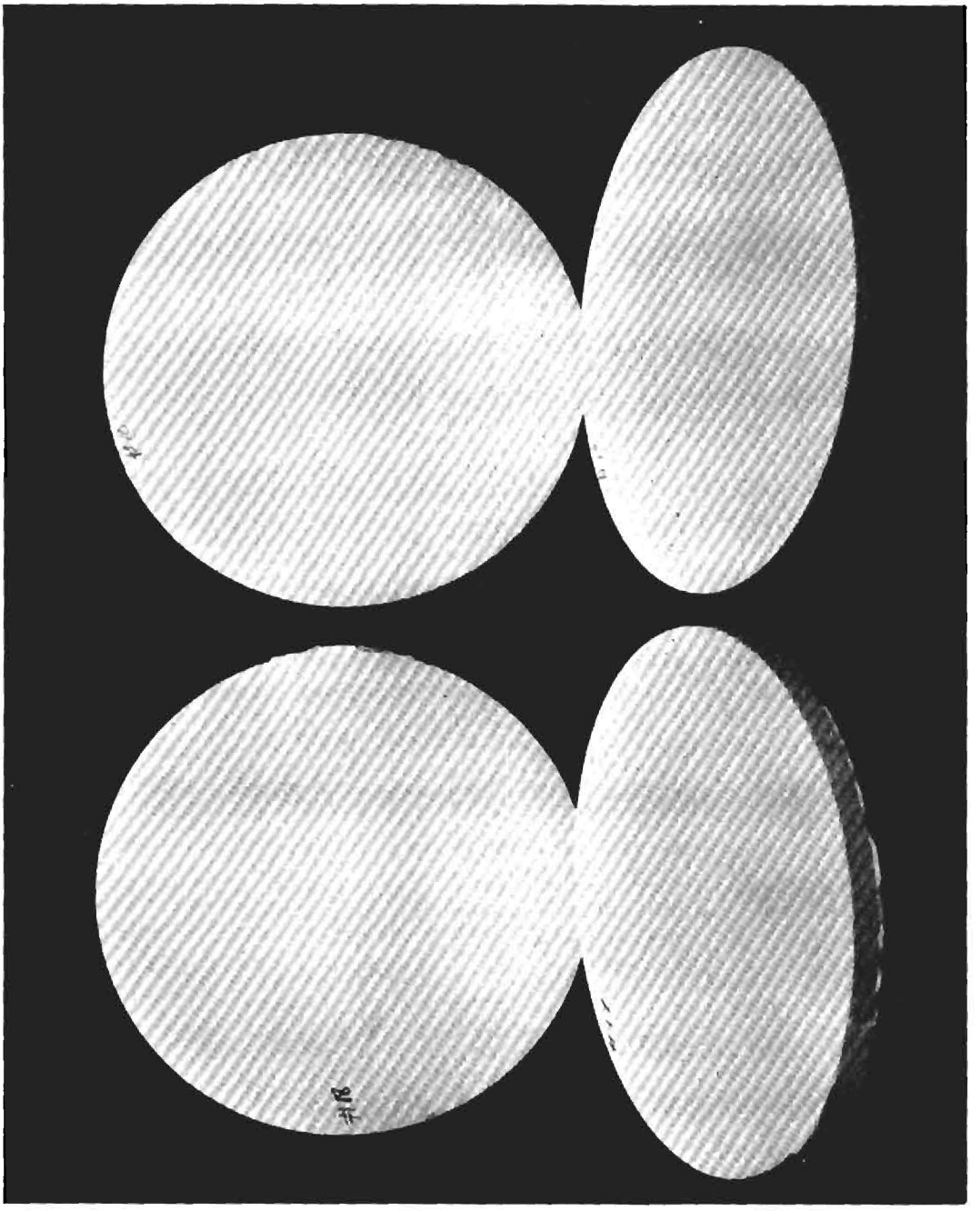


Figure 24. Slip-Cast Fused Silica Thermal Conductivity Test Specimens.

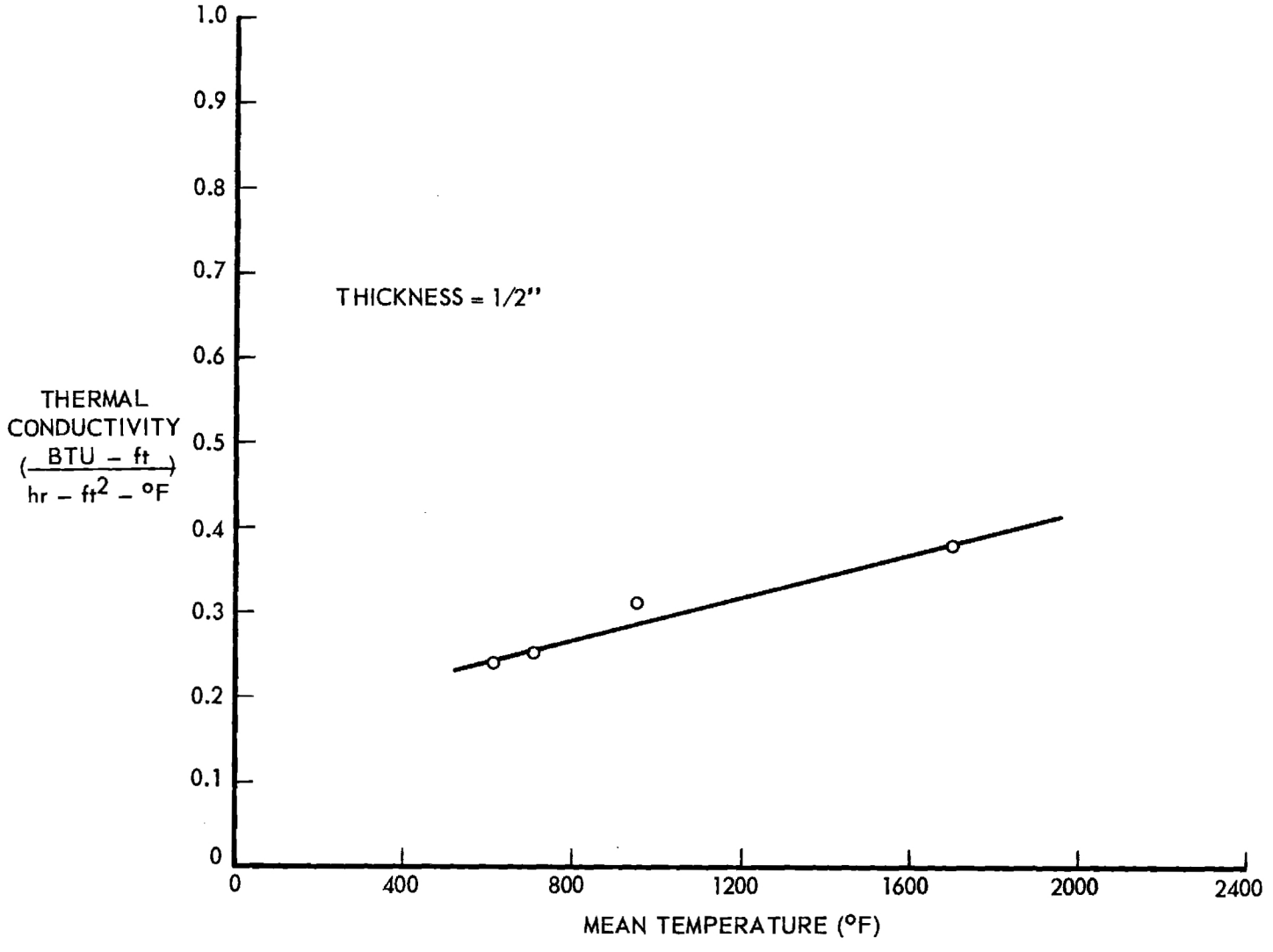


Figure 25. Effect of Temperature on Thermal Conductivity of a One-Half Inch Fused Silica Specimen.

The determination of a "maximum" error is listed below. This was calculated to be 5.6 per cent. This result is based only upon the possible errors in determining each of the terms used in the equation for calculating the thermal conductivity. Omitted from this result are the possibility of edge losses in the samples, incomplete contact with all the surfaces of the samples, small changes in room temperature, and small changes in the temperature of the incoming cooling water. These effects are assumed to be negligible.

The equation for calculating the thermal conductivity is

$$k_m = C \frac{E\ I}{2\ A} \quad \frac{T}{\Delta t} .$$

From this equation the total derivative is

$$dk_m = \frac{\partial k_m}{\partial E} \quad dE + \frac{\partial k_m}{\partial I} \quad dI + \frac{\partial k_m}{\partial T} \quad dT + \frac{\partial k_m}{\partial A} \quad dA + \frac{\partial k_m}{\partial(\Delta t)} \quad d(\Delta t)$$

$$dk_m = \frac{CI\ T}{2A\Delta t} \quad (dE) + \frac{CE\ T}{2A\Delta t} \quad (dI) + \frac{CE\ I}{2A\Delta t} \quad (dT) + (-1) \frac{CEI\ T}{2A^2\ \Delta t} \quad (dA)$$

$$+ (-1) \frac{CEI\ T}{2A(\Delta t)^2} \left[d(\Delta t) \right]$$

Upon factoring this becomes

$$dk_m = k_m \left[\frac{dE}{E} + \frac{dI}{I} + \frac{dT}{T} - \frac{dA}{A} - \frac{d(\Delta t)}{\Delta t} \right]$$

$$dk_m = \frac{dE}{E} + \frac{dI}{I} + \frac{dT}{T} - \frac{dA}{A} - \frac{d(\Delta t)}{\Delta t}$$

The error computed in this manner is a maximum when all the terms on the right add. Thus the maximum error can be expressed in the following

way:

$$\text{Maximum error} = \pm\left[\frac{dE}{E} + \frac{dI}{I} + \frac{dT}{T} + \frac{dA}{A} + \frac{d(\Delta t)}{\Delta t}\right].$$

In order to determine a numerical value from this expression, a value for the temperature drop, Δt, across the test samples must be assumed. The recommended minimum Δt of 30° is used in order for

$$\frac{d(\Delta t)}{(\Delta t)}$$

to be a maximum. The error in measuring both E and I is so small that it is neglected.

Substituting into the maximum error expression the numerical value of the possible error in each term yields:

$$\text{maximum error} = \pm \frac{.003}{.500} + \frac{1.5}{30} \times 100 \text{ per cent}$$

$$\text{maximum error} = \pm 5.6 \text{ per cent.}$$

E. Rocket Motor Test Facility

The Station's Ceramics Branch constructed a miniature oxyhydrogen rocket motor test facility during 1957. This was a combined effort by the Navy Bureau of Ordnance and the Station's Ceramics Branch. The primary purpose of this test facility is to evaluate materials for use in rocket motors, i.e., nozzles and jet vanes.

This facility was evaluated for possible use as a preliminary test device for screening various compositions to be tested by Redstone Arsenal's 4HT and 164HT burners. Comparison of data obtained for Micarta with Redstone Arsenal's facility and the Station's rocket motor test facility indicated that data obtained from the two facilities can be correlated. The maximum ablation rate

obtained with the Station's facility was approximately one-half the maximum ablation rate obtained by Redstone Arsenal with their 4HT and 164HT burners. This held true for large time limits, i.e., between 10 and 50 seconds. This ablation rate was determined by the thickness of the test sample and not the mass removed.

A sample holder was designed and constructed for mounting ablation rate test samples behind the Station's oxyhydrogen rocket motor. This sample holder can be seen in Figure 26. The holder was designed so that the sample can be placed at varying distances from the rocket motor and the angle of impingement of the exhaust flame can be varied from 45° to 90° with the sample pivoted about the point of flame impingement.

The ablation tests were conducted with samples which were 2 inches x 7 inches x 1/2 inch. Each sample was held at a 45° angle to the exhaust gases of the oxyhydrogen rocket motor. The sample holder utilized a spring-loaded thermocouple insulated on the rear of the sample to automatically record temperature changes with time on a strip chart recorder. This thermocouple was in contact with the backside of the sample directly opposite the center of the area struck by the exhaust gases. The sample was positioned so that the center of the area struck by the exhaust gases was 6 inches from the exit plane of the rocket motor.

The calculated exhaust gas conditions at the exit plane of the rocket nozzle are as follows:

Pressure = 15.1 psia

Velocity = 7966 ft/sec

Temperature = 3214° R

Mach No. = 2.5

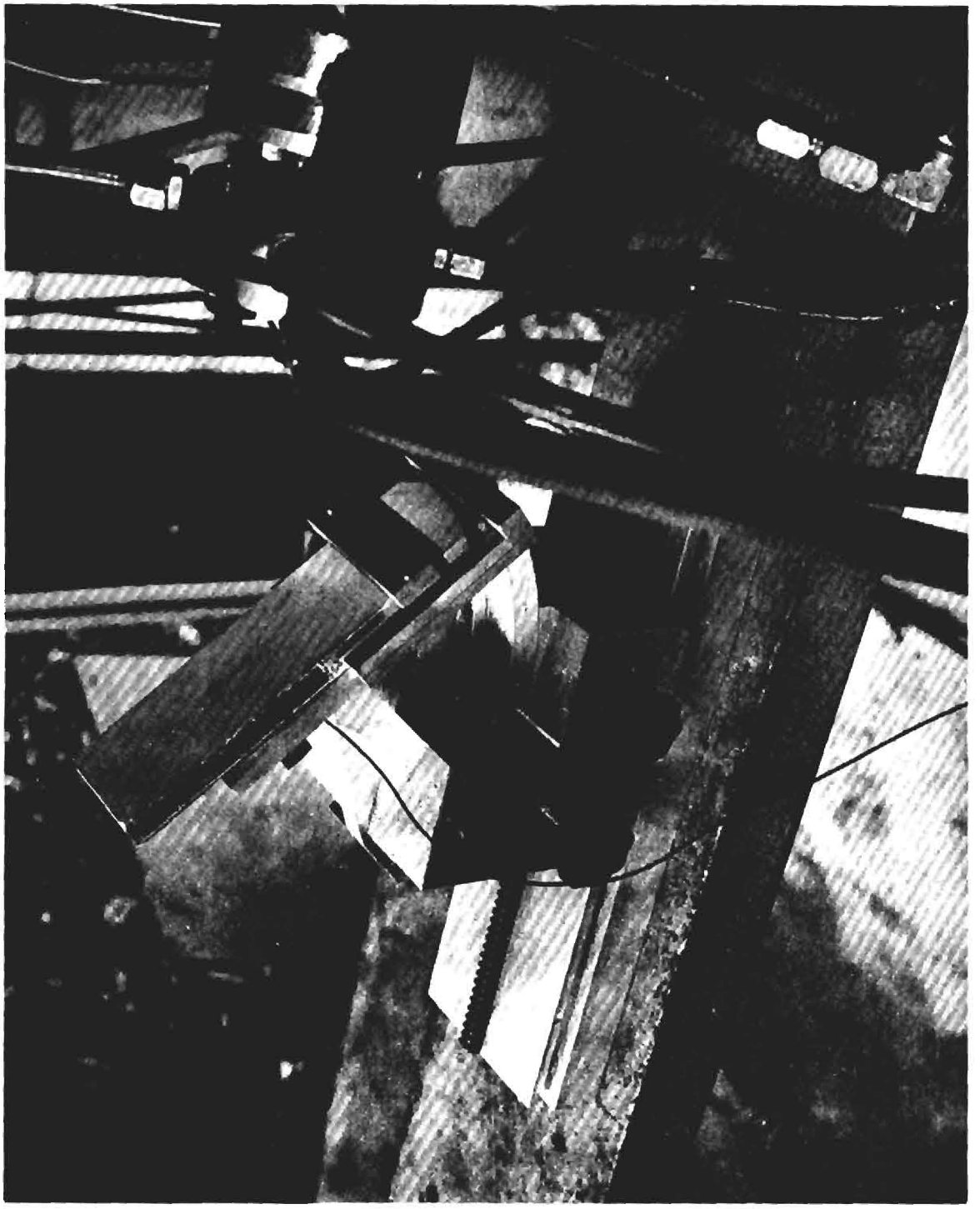


Figure 26. Sampler Holder for Ablation Studies.

These values were determined by using a oxygen-hydrogen weight ratio of 3.97, assuming a constant pressure (275 psi) combustion process between hydrogen and oxygen, and defining a mean ratio of specific heats as

$$\overline{K} = \frac{\Sigma N_{pi} K_i}{N_p} \qquad (i = 1, 2, --)$$

where

N_{pi} = Number of moles of a particular gas in combustion products

N_p = Total number of moles in combustion products

K_i = Ratio of specific heats of a particular combustion product.

At the position of the test sample the heat flux was 1150 $Btu/ft^2 sec$ measured with a water-cooled 3/8-inch-diameter copper tube on a one-inch length.

The ablation rates of each sample were determined by measuring the thickness of the sample before testing, substracting the minimum thickness after testing and dividing by the length of time the rocket motor was fired.

Cement-fused silica grain compositions similar to those sent to Redstone Arsenal for evaluation on their 4HT burner were fabricated and tested with the Station's rocket motor facility. As previously stated, the maximum ablation rate of the same samples tested with the Station's facility was approximately one-half the maximum ablation rate of Redstone Arsenal's 4HT burner. These results are tabulated in Table VII.

TABLE VII

PRELIMINARY ABLATION STUDIES OF HI-EARLY CEMENT AND FUSED SILICA MIXES

Sample No.	Hi-Early Cement (%)	-100 Mesh Fused Silica Grain (%)	Backside Δ T (° C)	Run Time (Sec)	Ablation Rate (In./Sec)
A1	14.8	59.3	0	12	.031
B1	16.7	57.4	0	12	.031
C1	18.5	55.6	0	12	.028
D1	20.2	53.9	0	12	.028
E1	22.2	51.9	0	12	.029

The ablation rate of these compositions was such that no change or increase in backside temperature was observed for the run period of 12 seconds. Figure 27 is a print of these test plates after being tested by the Station's burner.

Various compositions were evaluated with the Station's facility. These compositions included various sizes of fused silica grain with Hi-Early Portland cement, fired fused silica slip soaked in phosphoric acid and fired fused silica slip soaked in Shell No. 1310 Epon resin, powdered additions of copper and graphite to fused silica slip, and laminates of cast fused silica thin shells backed with fused silica foam.

Monofractions of fused silica grain were mixed with Hi-Early cement and water. The mixes were cast in waxed pasteboard boxes to form the sample size of 1/2 inch x 2 inches x 7 inches. The specimens were allowed to cure and dry before being tested. The results of the Station's burner test are listed in Table VIII.

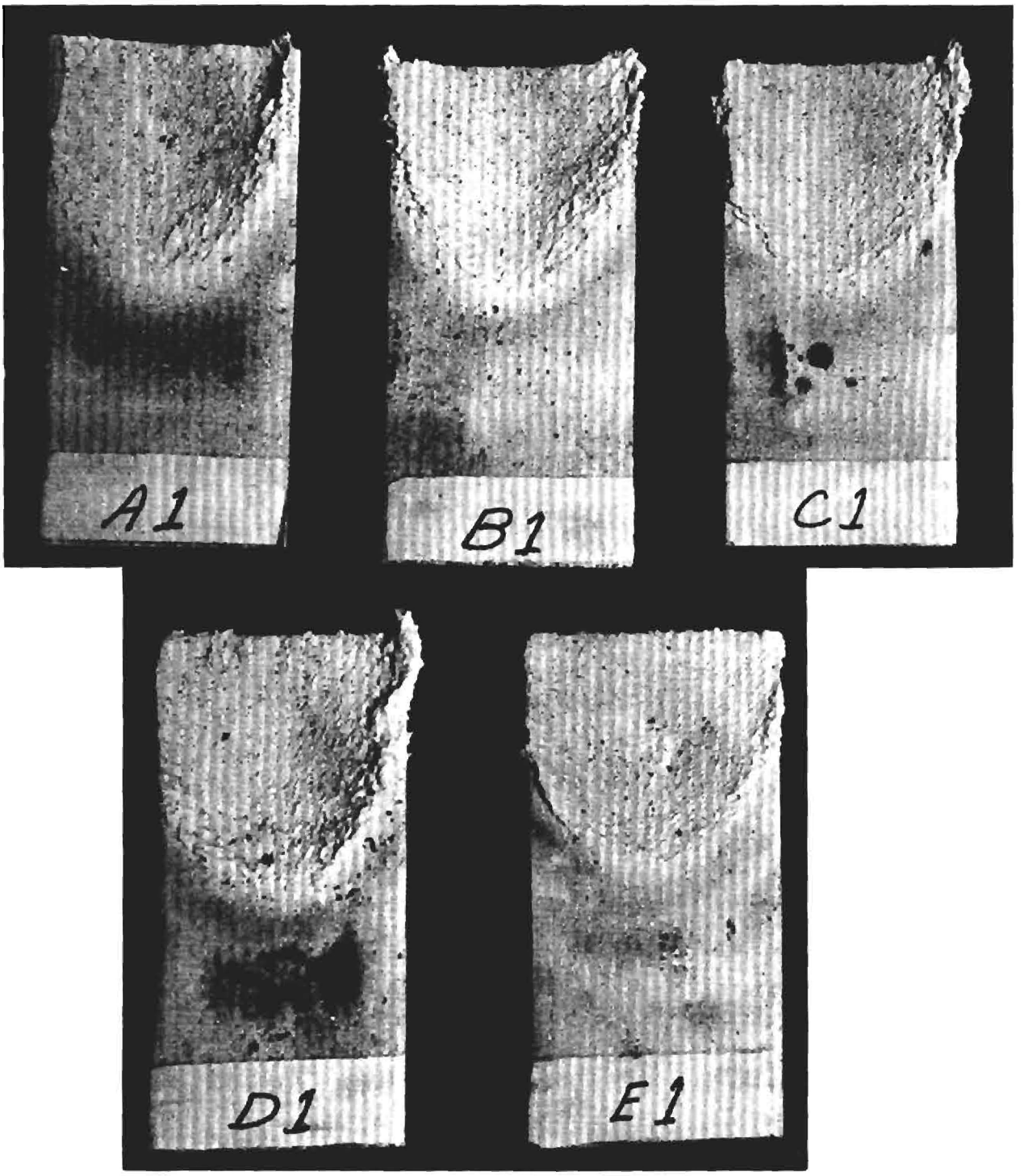


Figure 27. Preliminary Ablation Samples of Hi-Early Cement and Fused Silica Grain Mixes After Ablation Test.

TABLE VIII

ABLATION OF HI-EARLY CEMENT AND FUSED SILICA GRAIN MIXES

Sample No.	Hi-Early Portland Cement (%)	Fused Silica Grain Percentage	Fused Silica Grain Mesh	Water (%)	Ablation Rate (In./Sec)
A	17.8	53.6	-20+100	28.6	.021
B	17.8	53.6	-100+325	28.6	.026
C	17.8	53.6	-325	28.6	.030
D	17.8	53.6	-100(as rec'd)	28.6	.023
E	17.8	53.6	50% -30+100 50% -100+325	28.6	.020
F	10.7	60.7	-325	28.6	.014
G	10.7	60.7	-30+100	28.6	.004
H	10.7	60.7	50% -30+100 50% -100+325	28.6	--
I	10.7	60.7	-100+325	28.6	.023
J	10.7	60.7	-100	28.6	.035
K	16.67	57.4	-30+100	25.9	.043
L	16.67	57.4	-100+325	25.9	.039
M	16.67	57.4	-325	25.9	.036
N	16.67	57.4	-100	25.9	.037

All above compositions are duplicates of ones previously sent to Redstone.

Figures 28 and 29 are prints showing these samples after being run on the Station's burner. The hole that appears in Sample E of Figure 28 was caused by the spring-loaded thermocouple breaking through the thinnest section of the plate after the run was made.

Specimens were cast with fused silica slip dried at 230° F and fired at 2000° F for 2 hours. The specimens were then soaked by standard methods previously described and were refired as described in Table IX. It should be noted that the designation of Slip No. 10 is the suppliers' designation number and has no reference to a different type of fused silica slip.

TABLE IX

SOAKING PROCEDURES AND ABLATION TEST REMARKS FOR FUSED SILICA SAMPLES

	Composition	Ablation Rate (In./Sec)	Remarks
I.	No. 10 fused silica slip fired at 2000° F, phosphoric acid soaked by standard method, refired to 2000° F for 2 hours.	--	Fractured in less than 2 seconds.
II.	No. 10 fused silica slip fired one hour at 2000° F, soaked in Shell No. 1310 Epon resin and cured at 480° F for 2 hours.	--	Burned through in less than 3 seconds. Sample appeared to have exfoliated
III.	No. 10 fused silica slip fired one hour at 2000° F.	None	Surface appeared slightly bubbled after a 20-second run.

The tested samples are shown in Figure 30. The fused silica-phosphoric-acid-soaked test plate failed due to thermal shock. The resin-soaked sample appeared to exfoliate during the test run. The untreated fused silica test plate exhibited no appreciable change, except a very slight bubbling of its

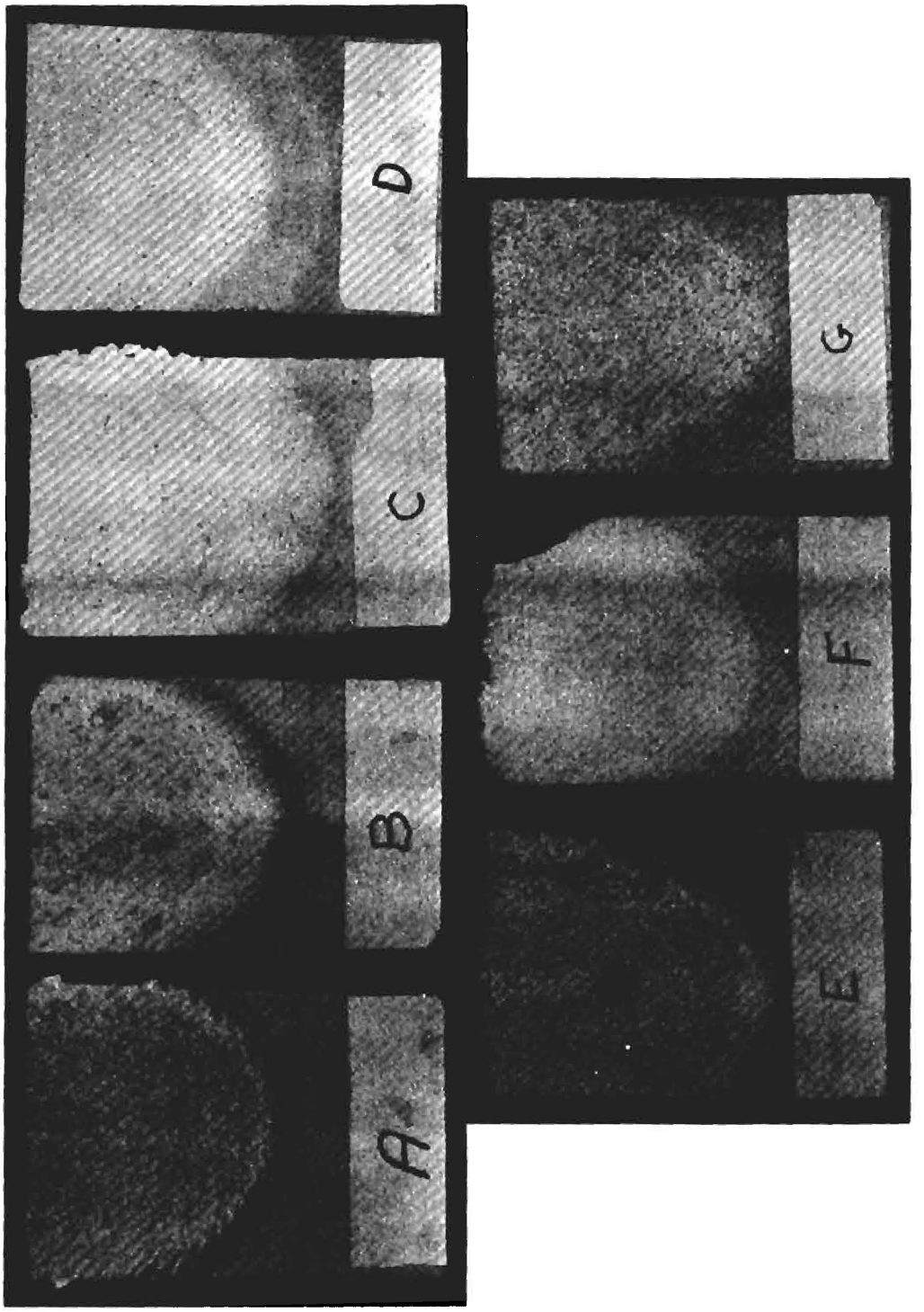


Figure 28. Hi-Early Cement--Fused Silica After Ablation Test.

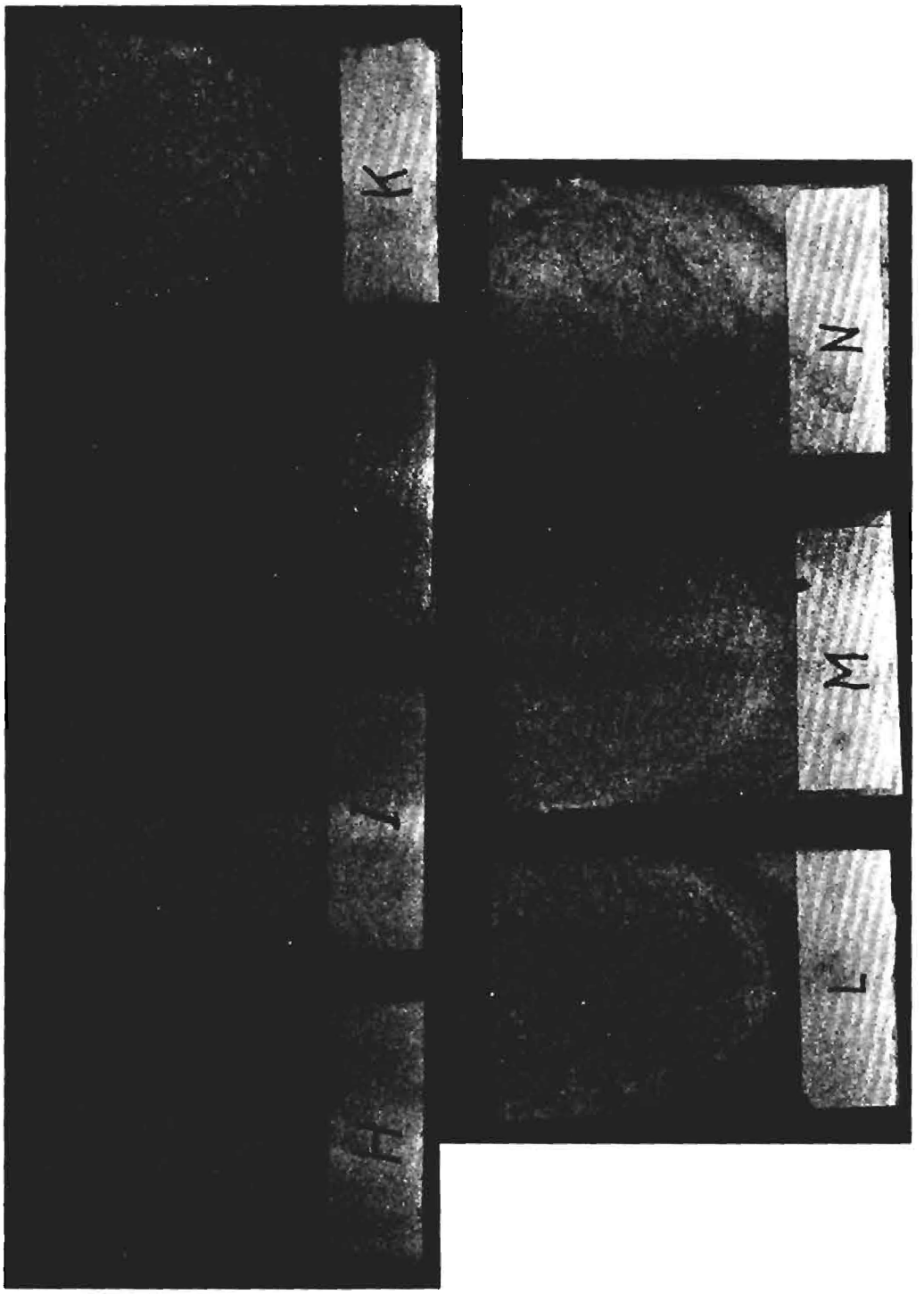


Figure 29. Hi-Early Cement--Fused Silica After Ablation Test.

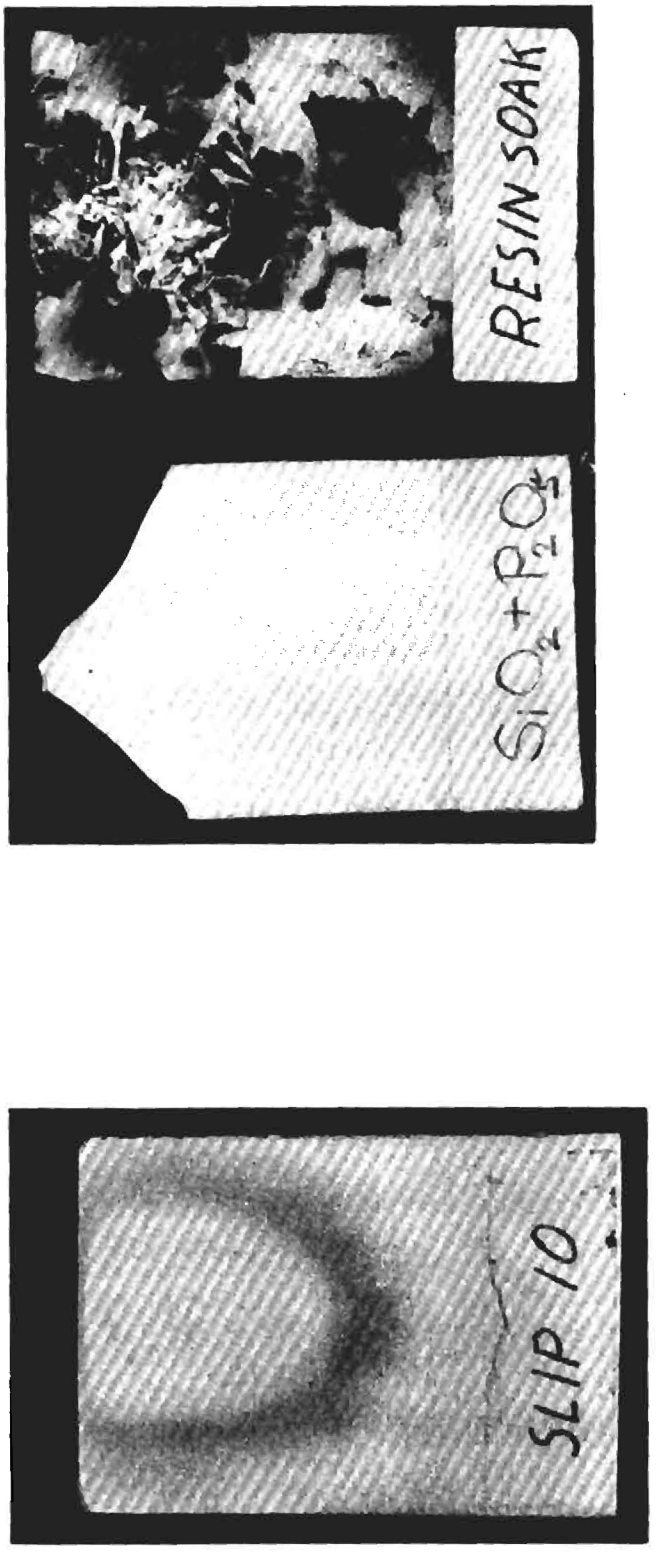


Figure 30. Comparison of Untreated Fused Silica with Phosphoric Acid-Soaked and Resin-Soaked Fused Silica After Ablation Test.

surface. Figure 31 compares the tested, untreated fused silica sample with one not tested.

Additions of 3, 5, 10 and 15 per cent by dry weight of Dixon's Microfyne and No. 2 flake graphite to fused silica slip were made. The per cent solids of the slip was held constant. The cast specimen was fired at 1800° F for 2 hours in an inconel firing box. The specimen was covered with lampblack and carbon dioxide gas was bled into the firing box during the entire firing cycle. Back-side temperature and ablation rates were determined. These results are shown in Table X.

TABLE X

ABLATION OF GRAPHITE ADDITIONS TO FUSED SILICA

Sample	Microfyne Graphite (%)	No. 2 Flake Graphite (%)	Run Time (Sec)	Backside Δ T (° C)	Ablation Rate (In./Sec)
AE-1	--	3	39.1	42	.001
AF-1	--	5	40.9	36	.001
AG-1	--	10	35.9	46	.001
AH-2	--	15	32.7	50	.001
AI-2	3	--	46.7	20	0
AJ-1	5	--	45.3	14	.001
AK-1	10	Could not cast specimen			
AL-1	15	Could not cast specimen			

Figure 32 shows the graphite--fused silica test plates after being tested by the Station's burner.

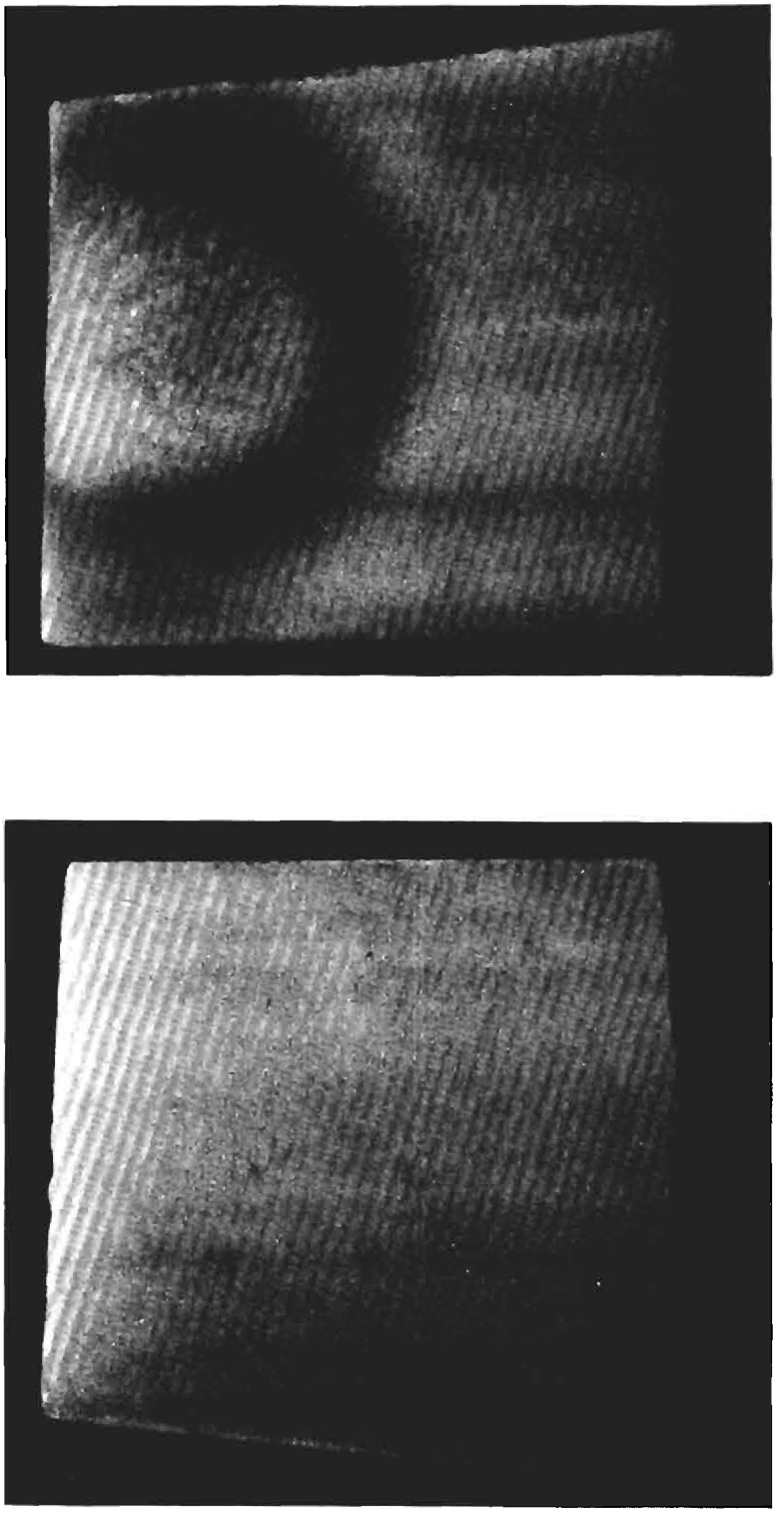


Figure 31. Comparison of Fused Silica Before and After Ablation Test. Run Time, 20 seconds.

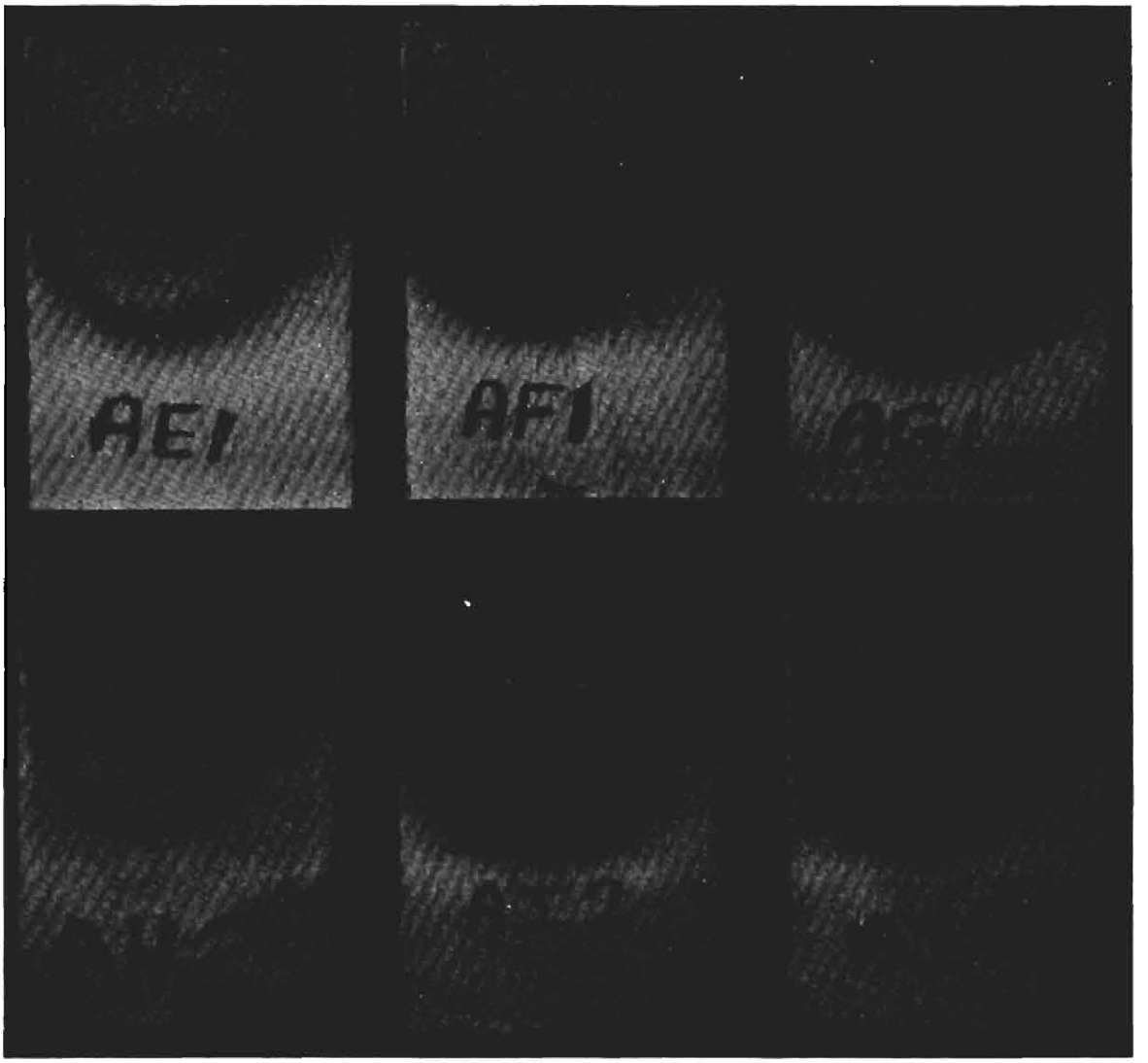


Figure 32. Graphite--Fused Silica After Ablation Tests.

Additions of 1, 3, 5, and 10 per cent by dry weight of Dixon's Microfyne and No. 2 flake graphite were made to fused silica slip. The per cent solids of the slip was held constant. Thin shells, 1/8- to 3/16-inch, were cast into the 1/2- x 2- x 7-inch shape and the shells were then filled with fused silica slip which was allowed to cast solid. This produced a laminated section. The test plates were fired in the same manner as the graphite additions previously described. The results for the laminated graphite sections are shown in Table XI.

TABLE XI

ABLATION OF GRAPHITE LAMINATE FUSED SILICA

Sample	Microfyne Graphite (%)	No. 2 Flake Graphite (%)	Run Time (Sec)	Backside Δ T (° C)	Ablation Rate (In./Sec)
P-2	--	1	39.3	26	0.002
Q-2	--	3	11	0	0.001
R-2	--	5	42.3	28	0.001
S-1	--	10	20.9	31	0.001
T-1	1	--	15.6	0	0
U-1	3	--	44.2	35	0.001
V-1	5	--	47.3	19	0
W-1	10	Could not cast specimen			

The test plates are shown in Figure 33 for the graphite laminated fused silica compositions.

Additions of 1, 3, 5, and 10 per cent by dry weight of Metals Disintegrating Company's MD 105 powdered copper were made to fused silica slip. The per cent

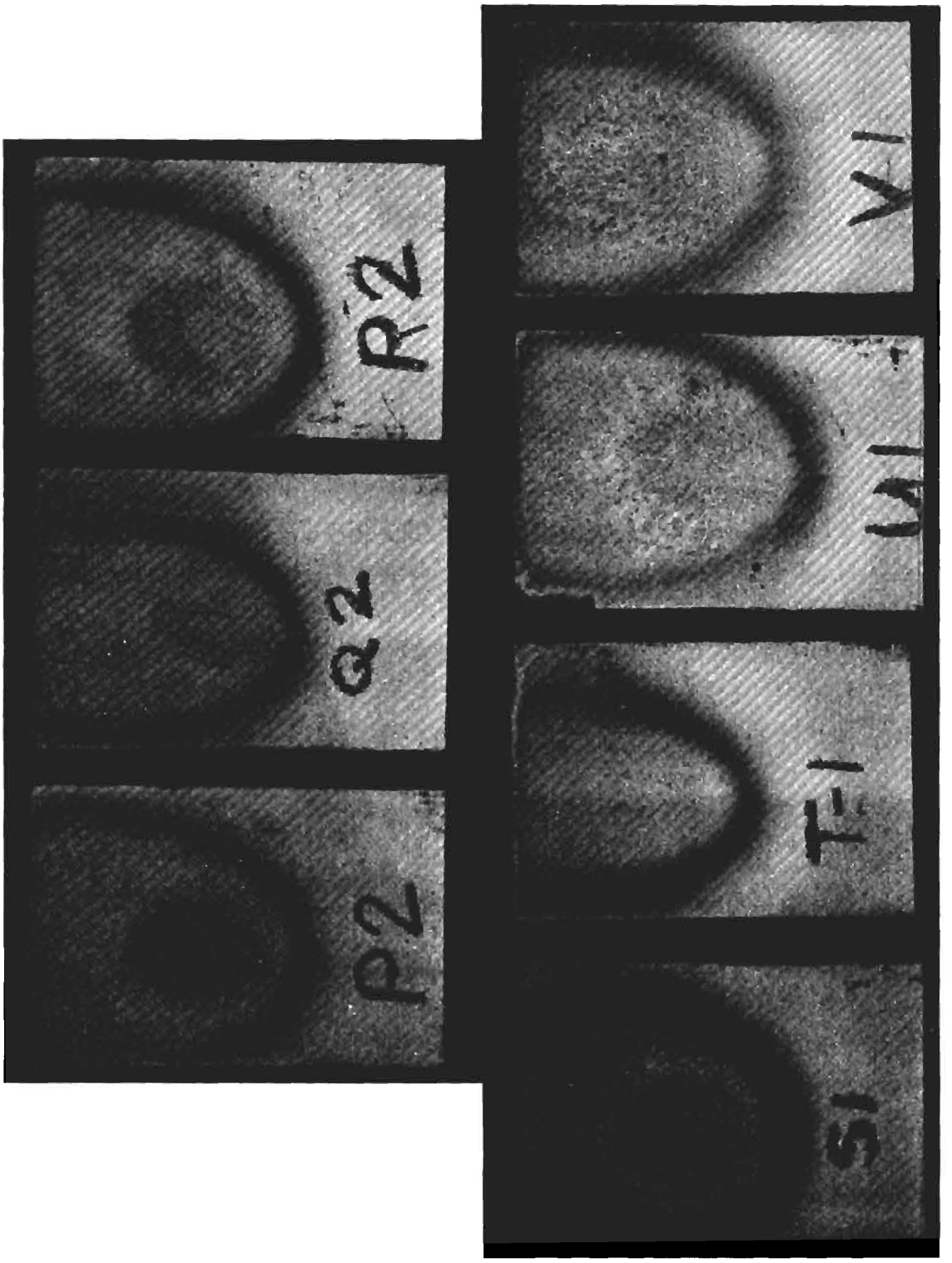


Figure 33. Graphite Laminate Fused Silica After Ablation Tests.

solids of the slip was held constant. Thin shells, 1/8- to 3/16-inch, were cast into the 1/2- x 2- x 7-inch shape and the shells were then filled with fused silica slip which was allowed to cast solid. The test plates were fired in the same manner as the graphite additions previously described. Results are shown in Table XII.

TABLE XII

ABLATION OF COPPER LAMINATE FUSED SILICA

Sample No.	Powdered Copper (%)	Run Time (Sec)	Backside Δ T (° C)	Ablation Rate (In./Sec)
AA1	1	45	14	.001
AB1	3	48.5	10	.001
AC1	5	51	8	.002
AD1	10	68	14	.001

The test plates are shown in Figure 34 for the copper laminate fused silica.

Figure 35 is a plot of the backside temperature versus run time of the burner on the copper laminate samples. The displacement of the curves to the right by increasing per cent copper results from the increase in mass of the sample. The best illustration of the effect of increasing per cent copper is obtained by comparing curves AA1 and AD1. The one-per-cent-copper sample required 30 seconds before a change occurred in backside temperature whereas the 10-per-cent-copper sample required 45 seconds. The flatness of the 10-per-cent-copper curve compared to the one-per-cent-copper curve suggests that the primary effect of increasing copper content on heat-conducting properties

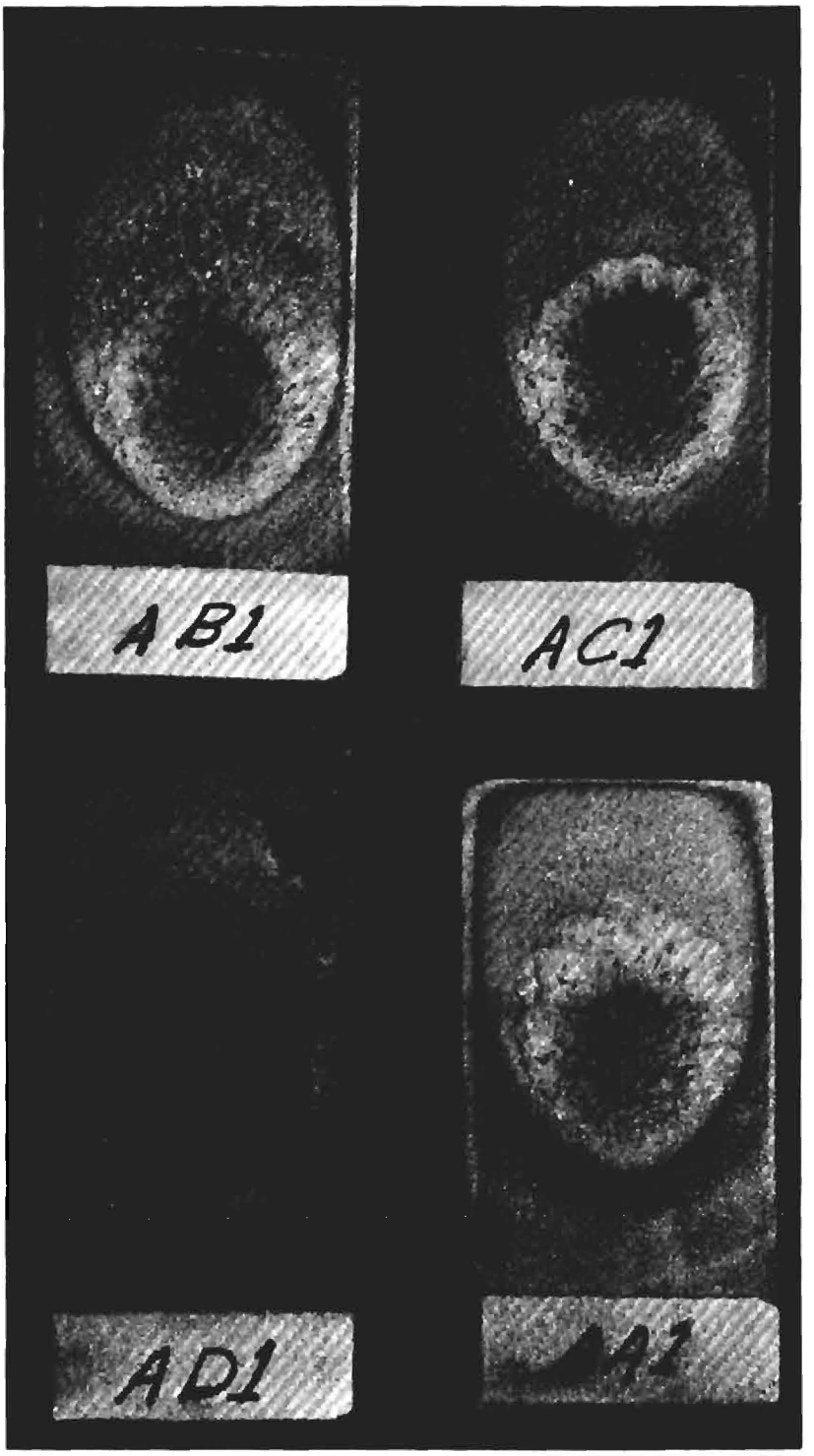


Figure 34. Copper Laminate Fused Silica After Ablation Tests.

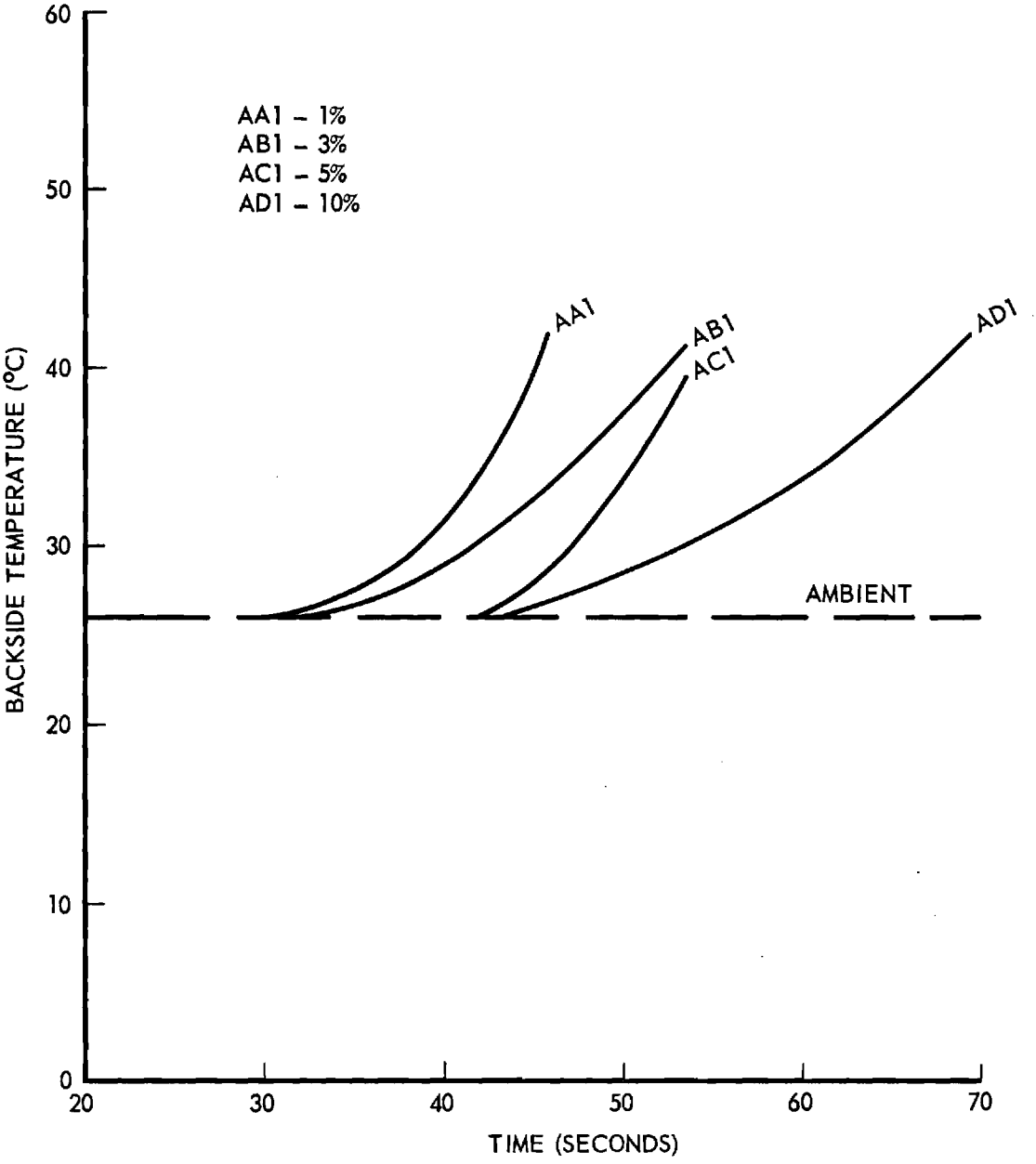


Figure 35. Effect of Backside Temperature of Copper Laminate Fused Silica with Time of Ablation Test.

is to decrease the thermal diffusivity. In other words, the thermal conductivity does not increase nearly as rapidly as does density with additions of copper.

Since the slip-cast fused silica did not tend to ablate to any large extent, it was considered that one way to further lower the backside temperature would be to form a laminate of a thin section of slip-cast fused silica which would be backed with a material that exhibited higher thermal insulating properties than slip-cast fused silica. Of course, the back-up material should be compatible, thermal expansion wise, with fused silica. The Glasrock Corporation had developed such a material which consisted of foamed fused silica slip.

Thin shells, approximately 1/8 inch thick, of the 1/2- x 2- x 7-inch shape were cast from fused silica slip. The shells were allowed to air dry, the cavity was coated with a 50-50 mixture of fused silica slip and Ludox LS colloidal silica, and then a desired liquid fused silica foam was spatulated into the cavity. The thin shell laminate was dried at 230° F and fired at 2100° F for 2 hours. The foam was prepared by whipping a suitable foaming agent into a stiff foam, and folding the foam into the fused silica slip. Small quantities of phosphoric acid, 35- to 40-per-cent-concentration, were added to the foam to improve its green and fired strength. The foaming agent used was Liquifoam which was supplied by the Glasrock Corporation. The following compositions listed in Table XIII were used in the fabrication of the foam laminates. Table XIV gives the backside temperature measurements of these compositions.

These tested specimens are shown in Figure 36. The burner flame undercut the thin shell of sample B1 just before the run stopped and caused it to peel back.

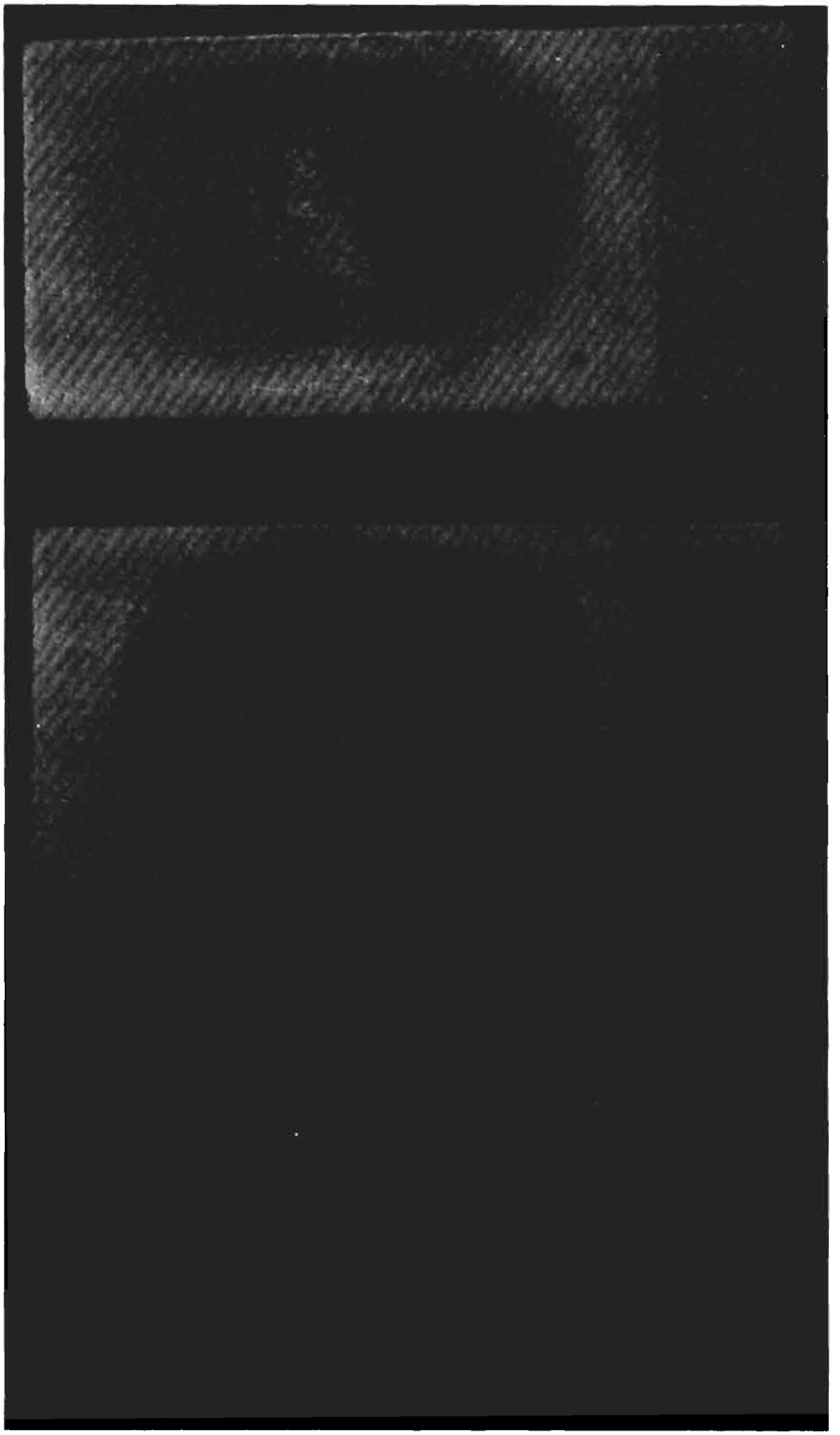


Figure 36. Foam Laminate After Ablation Tests.

TABLE XIII

FOAM LAMINATE COMPOSITIONS

Sample No.	Compositions		
	Fused Silica Slip (Ml)	Foaming Agent (Ml)	Phosphoric Acid (Ml)
A1	200	100	1
B1	300	100	1
C1	200	100	3

TABLE XIV

BACKSIDE TEMPERATURE MEASUREMENTS OF FOAM LAMINATE COMPOSITIONS

(ΔT of Backside Temperature)

Run Time (Sec)	Sample A1 (° C)	Sample B1 (° C)	Sample C1 (° C)
0 to 20	0	0	0
25	0	0.5	8.0
30	1.0	3.0	24.0
35	6.0	7.0	-
40	16.0	14.0	-
45	-	24.0	-
50	-	-	-

Figure 37 is a plot of backside temperature versus run time. The effect of small changes in density of the foam silica on backside temperature is slight as indicated by curves A1 and B1 of Figure 37, the latter being the more dense. The addition of acid which significantly affects the particle-to-

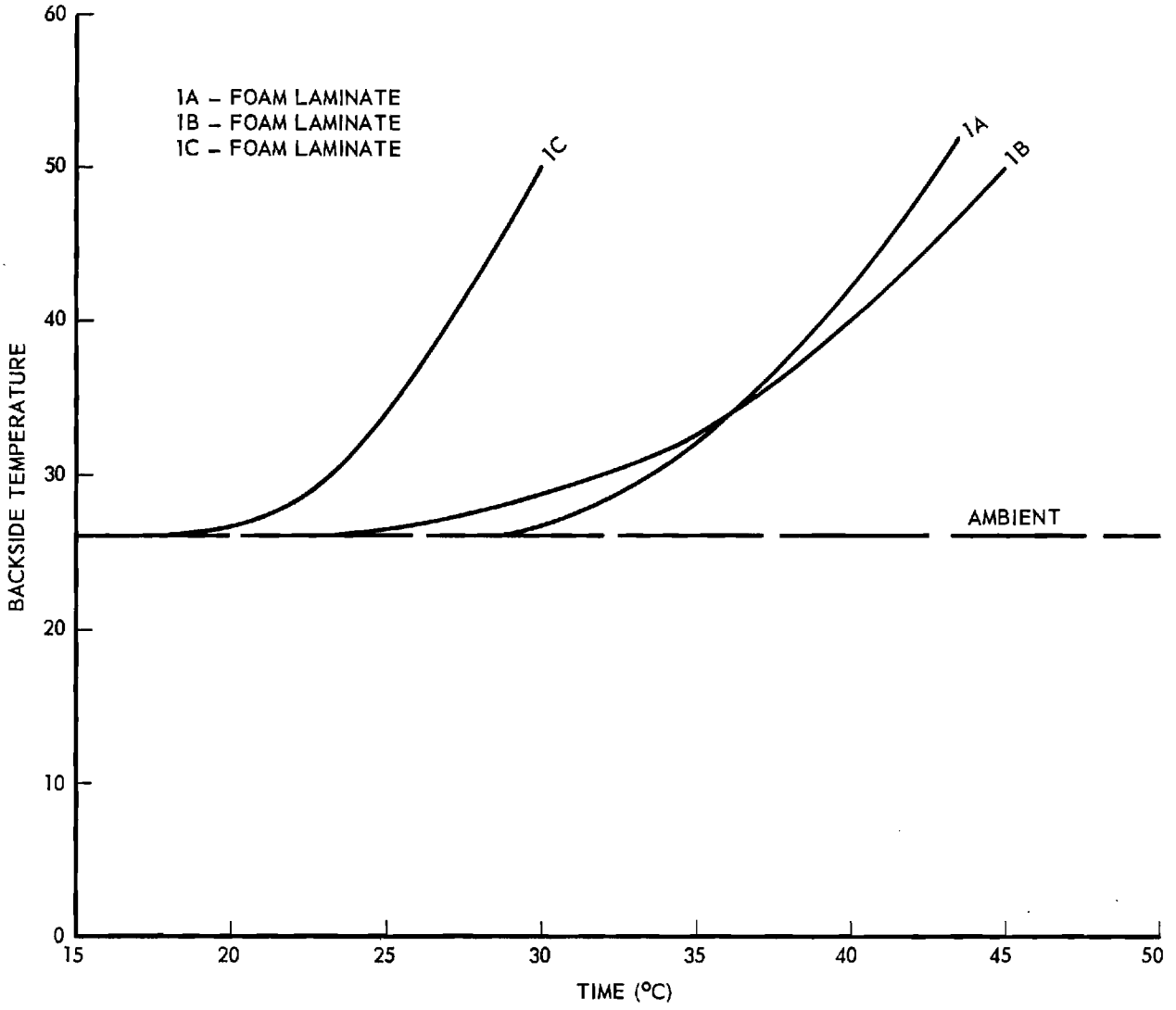


Figure 37. Effect of Backside Temperature of Foam Laminates with Time of Ablation Test.

particle bond increased the heat conduction properties of the material. This is indicated by the quick rise in backside temperature, Figure 37, curve C1, compared to the somewhat slower rise shown in A1.

The time required for a significant backside temperature increase of the foam laminates did not vary greatly from that required for a solid sample. This is explained by the fact that although the thermal conductivity of the foam is much lower than the solid body, the density is much lower also. Thus, the thermal diffusivity, $\frac{K}{\rho C_p}$, of the foam could be larger than that of the solid slip-cast material.

F. Test Samples for Evaluation by Redstone Arsenal and Other Agencies

At the request of the sponsor test samples were fabricated from fused silica and forwarded to several agencies for the purpose of obtaining electrical, thermal and other such properties associated with short time, high heat fluxes in high velocity gas streams.

Two-inch-diameter waffers were dry pressed to a total pressure of 4.5 tons using one milliliter of Ludox LS colloidal silica to 10 grams of dry material. The compacted waffers were fired at 1800° F for one hour, soaked in Ludox LS colloidal silica and refired at 1800° F for one hour. These waffers were sent to Diamond Ordnance Fuse Laboratories for electrical measurements and are listed in Table XV as A-1, B-1, C-1 and D-1. Composition A-2 was slip cast in a waxed cardboard mold. The slip was prepared from -16+30 mesh fused silica grain milled for 96 hours with 20 per cent water. B-2, C-2, and D-2 are Hi-Early Portland cement, fused silica grain, and water compositions mixed into a good trowling mix before casting in waxed cardboard molds. The properties for these are also found in Table XV.

TABLE XV

ELECTRICAL PROPERTIES OF FUSED SILICA COMPOSITIONS
TESTED BY DIAMOND ORDNANCE FUSE LABORATORIES

Sample No.	Composition	Dielectric Constant		Dissipation Factor	
		10^7 Cycles/Sec	10^8 Cycles/Sec	10^7 Cycles/Sec	10^8 Cycles/Sec
A-1	-31+100 mesh fused silica	2.77	2.76	.00149	.00121
B-1	-100 mesh fused silica	2.65	2.64	.00247	.00288
C-1	90% -30+100 mesh fused silica, 10% Ky. Old Mine No. 4 ball clay	3.01	2.98	.00536	.00482
D-1	90% -100 mesh fused silica, 10% Ky. Old Mine No. 4 ball clay	2.80	2.78	.00615	.00482
A-2	100% fused silica	2.68	2.68	.00196	.00168
B-2	14.7% Hi-Early cement 59.0% -100 mesh fused silica, 26.3% water	2.73	2.70	.00373	.00364
C-2	18.5% Hi-Early cement 55.5% -100 mesh fused silica, 26% water	3.11	3.07	.00990	.00572
D-2	22.5% Hi-Early cement, 52.5% -100 mesh fused silica, 25% water	2.78	2.75	.00913	.00542

Samples of slip-cast fused silica fired at 1800° F for one hour were submitted to Melpar, Inc. for electrical measurements at various temperatures. Table XVI lists the results:

TABLE XVI

EFFECT OF TEMPERATURE ON ELECTRICAL PROPERTIES OF SLIP-CAST FUSED SILICA†

Temperature (° F)	Dielectric Constant	Loss Tangent
75	3.17	0.0002
1500	3.18	0.0006
2015	3.28	0.007
2500	3.42	0.012

†Tested by Melpar, Inc. at 10^{10} cycles/sec.

It must be noted at this point that any measurements made above 2000° F are measurements of fused silica--cristobalite combinations. Above this temperature cristobalite crystallizes from fused silica and increases with time and temperature. The specimen at 2500° F therefore was probably predominately if not entirely cristobalite.

Slip-cast fused silica specimens of the type shown in Figure 38 were prepared and fired to 2000° F and held for 2 hours. The specimens were sent to Midwest Research Institute for thermal conductivity determinations. The results for one specimen are shown in Figure 39. The steep rise in thermal conductivity above 2000° F for this specimen is due to the formation of cristobalite. This specimen was above 2000° F for over one week. X-ray analysis after test showed almost complete conversion of fused silica to cristobalite and the absence of quartz and tridimite.

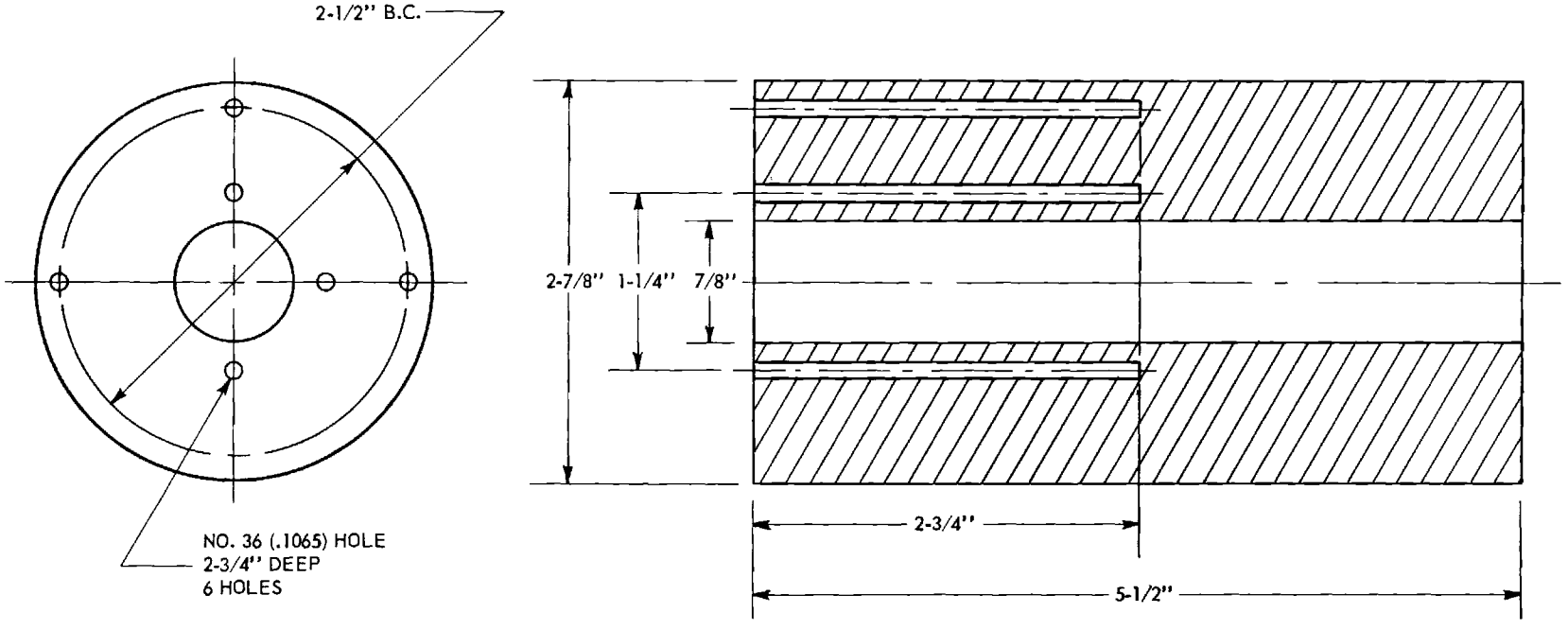


Figure 38. Thermal Conductivity Test Specimen Design Sent to Midwest Research Institute.

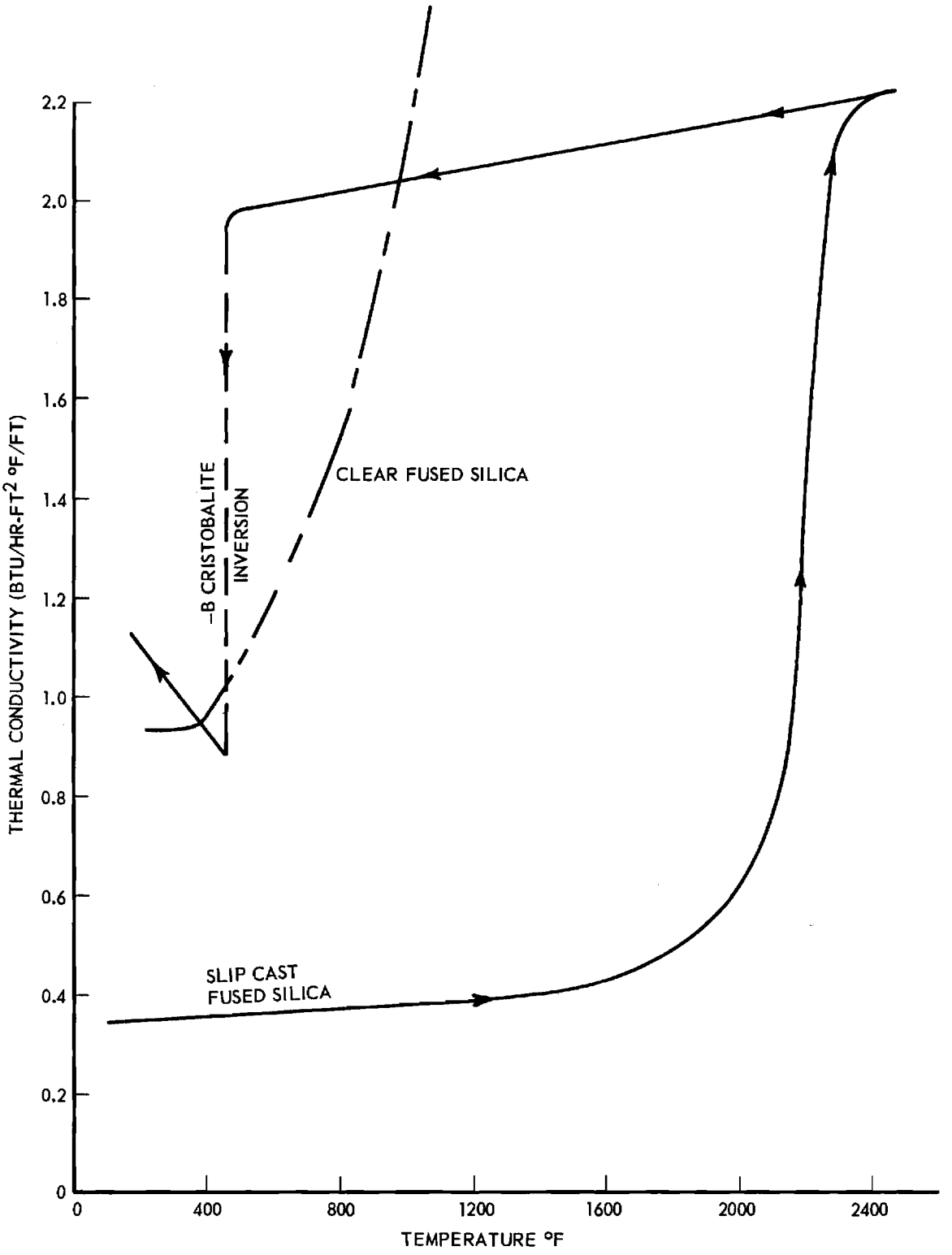


Figure 39. Effect of Temperature and Thermal Conductivity on Slip-Cast Fused Silica Sent to Midwest Research Institute.

Test samples of fused silica and fused silica compositions were sent to Redstone Arsenal for evaluation on their 4HT and 164HT burners. The two types of specimens are a burner test plate and a nose cone configuration of design shown in Figure 40. A list of the compositions and fabrication techniques for both the designs are shown in Table XVII and Table XVIII.

TABLE XVII

NOSE CONE CONFIGURATION SAMPLES
SUPPLIED TO REDSTONE ARSENAL

Ga. Tech Number	Composition	Fabrication Techniques
Preliminary	-30+100 mesh fused silica grain; colloidal silica	Semislip grain--colloidal silica mixture cast in waxed cardboard mold; fired at 1800° F for one hour; soaked in 30% solids colloidal silica solution; refired at 1800° F for one hour.
2-3-NC	100% fused silica	Slip cast from fused silica slip; fired at 1800° F for one hour.
2-4-NC	95% fused silica 5% Ky. Old Mine #4 ball clay	Slip cast in plaster mold (Keltex-treated), fired from room temperature to 2000° F; held 1/2 hour, air quenched.
2-5-NC	100% fused silica	Slip cast from fused silica slip; fired at 1800° F for one hour.
3-7-NC	95% fused silica 5% Ky. Old Mine #4 ball clay	Slip cast; fired from room temperature to 2000° F; held 1/2 hour; air quenched.

Small test samples 1/2 inch in diameter by 2 inches long with a rounded nose were prepared and tested in a plasma jet experimental wind tunnel at GIANNINI RESEARCH LABORATORY. Samples of pure fused silica and 95 per cent fused silica and 5 per cent graphite were prepared by slip casting. The test pieces were fired at 2000° F with the samples containing graphite being shrouded in lampblack.

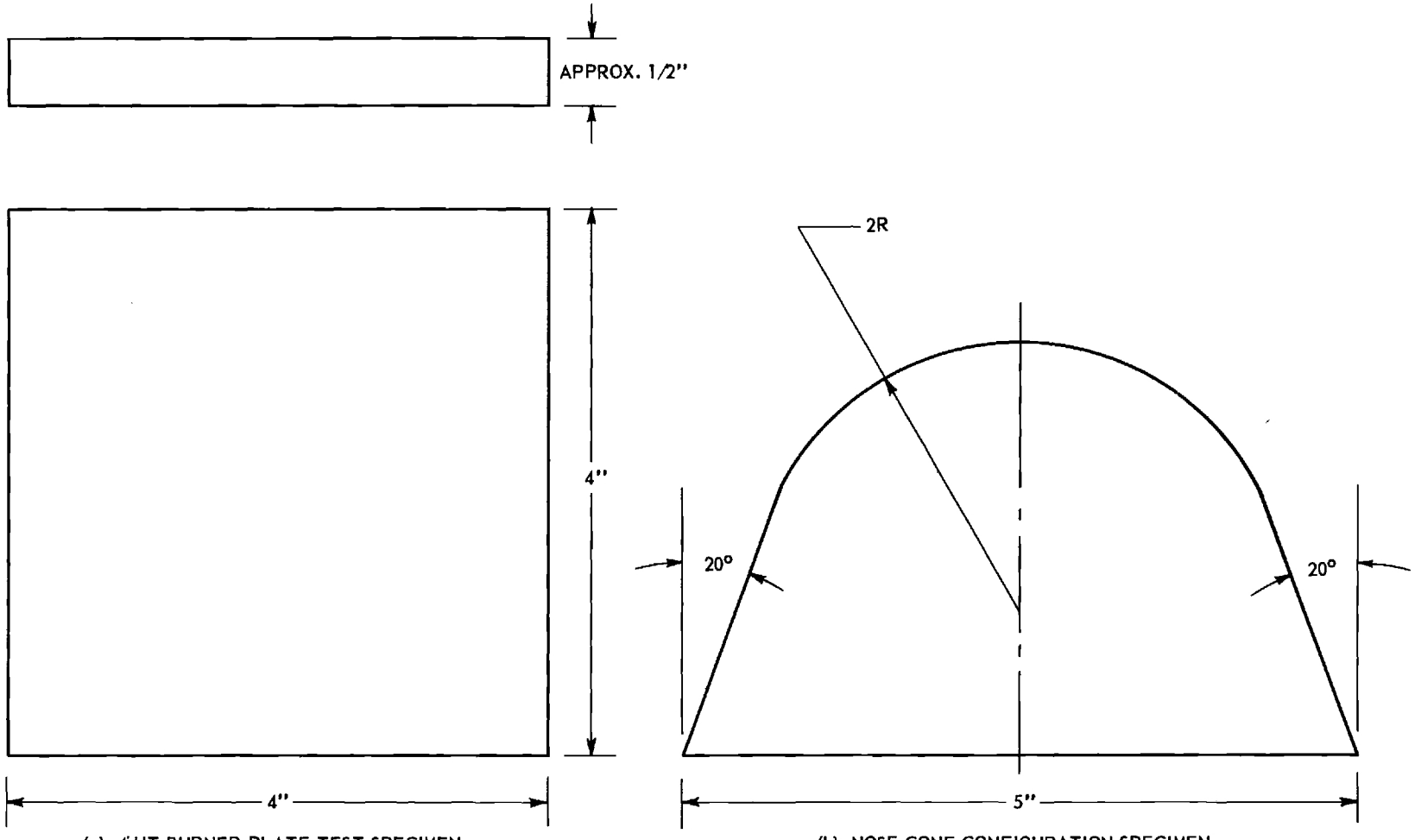


Figure 40. Design of Burner Test Plate and Nose Cone Configuration of Samples Sent to Redstone Arsenal.

TABLE XVIII

BURNER TEST PLATE SAMPLES SUPPLIED TO REDSTONE ARSENAL

Ga. Tech Number	Composition	Fabrication Technique
Preliminary	-30+100 mesh fused silica grain; colloidal silica	Semislip grain--colloidal silica mixture cast in waxed cardboard mold; fired at 1800° F for 1 hour, soaked to saturation in 30% colloidal silica solution; refired at 1800° F for 1 hour.
4	-100 mesh fused silica grain; colloidal silica	Semislip grain--colloidal silica mixture cast in waxed cardboard mold; fired at 1900° F for 30 minutes; soaked in colloidal silica solution; refired at 1900° F for 30 minutes.
7	-100 mesh fused silica grain; colloidal silica	Semislip grain--colloidal silica mixture cast in waxed cardboard mold, fired at 1900° F for 30 minutes; soaked in colloidal silica solution; refired at 1900° F for 30 minutes.
8	-325 mesh fused silica grain; colloidal silica	Semislip grain--colloidal silica mixture cast in waxed cardboard mold, fired at 1900° F for 30 minutes, soaked in colloidal silica solution, refired at 1900° F for 30 minutes.
S-5	95% fused silica 5% Ky. Old Mine #4 ball clay	Slip cast in Keltex-treated plaster mold, fired from room temperature to 2000° F; held for 1/2 hour; air quenched.
S-10	100% fused silica	Acid-treated fused silica slip (8 ml of 1.16N HCl solution per gallon slip), slip pH approximately 2.5; deaired before casting; fired from room temperature to 2000°F; held for 1/2 hour; air quenched.
3-8-4HT	Shell: 5% graphite 95% fused silica Core: 100% fused silica	Laminated cast: Graphite--fused silica slip cast to obtain shell approximately 1/8 inch thick; dumped; finished casting solid with straight fused silica slip. Fired in lampblack to 1900° F; soaked in colloidal silica; refired in lampblack to 1900° F.
	Shell: 15% graphite 85% fused silica Core: 100% fused silica	
3-9-4HT	Shell: 15% graphite 85% fused silica Core: 100% fused silica	

(Continued)

TABLE XVIII (Continued)

BURNER TEST PLATE SAMPLES SUPPLIED TO REDSTONE ARSENAL

Ga. Tech Number	Composition	Fabrication Technique
13-14-A	Shell: 1% graphite 99% fused silica Core: 100% fused silica	Laminated cast: Cast same as 3-8-4HT and 3-9-4HT fired to 1800° F in lampblack; held for 2 hours.
13-14-C	Shell: 5% graphite 95% fused silica Core: 100% fused silica	
13-14-D	Shell: 10% graphite 90% fused silica Core: 100% fused silica	
13-14-G	Shell: 3% copper 97% fused silica Core: 100% fused silica	Laminated cast: Copper--fused silica slip cast to obtain shell approximately 1/8 inch thick; dumped; funished casting solid with straight fused silica slip. Fired to 1800° F in lampblack; held for 2 hours.
6-10-A	14.8% Hi-Early cement 59.3% -100 mesh fused silica 25.9% water	Cement and fused silica grain were dry mixed thoroughly, water added and then remixed until plastic. Samples were cast in waxed cardboard molds and allowed to set for 16 hours, then covered with damp rag (kept damp) for 72 hours. Samples were not fired.
6-10-B	16.7% Hi-Early cement 57.4% -100 mesh fused silica 25.9% water	
6-10-C	18.5% Hi-Early cement 55.6% -100 mesh fused silica 25.9% water	
6-10-D	20.2% Hi-Early cement 53.9% -100 mesh fused silica 25.9% water	
6-10-E	22.2% Hi-Early cement 51.9% -100 mesh fused silica 25.9% water	

(Continued)

TABLE XVIII (Continued)

BURNER TEST PLATE SAMPLES SUPPLIED TO REDSTONE ARSENAL

Ga. Tech Number	Composition	Fabrication Technique
6-10-F	18.5% Hi-Early cement 18.5% -4+16 mesh fused silica 18.5% -16+30 mesh fused silica 18.5% -30+100 mesh fused silica 26.0% water	
12-13-A	25% Hi-Early cement 75% -30+100 mesh fused silica 35% water (based on dry weight)	Cement and fused silica grain were dry mixed thoroughly, water added and then remixed until plastic. Cast in cardboard molds and allowed to set in moist air for 1 day and under water from 3 to 5 days, then air dried for one week. Not fired.
12-13-C	25% Hi-Early cement 37.5% -30+100 mesh fused silica 37.5% -100+325 mesh fused silica 35% water (based on dry weight)	
12-13-E	25% Hi-Early cement 75% -100+325 mesh fused silica 35% water (based on dry weight)	
12-13-H	25% Hi-Early cement 75% -100 mesh fused silica 35% water (based on dry weight)	
12-13-J	40% Hi-Early cement 60% -325 mesh fused silica 40% water (based on dry weight)	

(Continued)

TABLE XVIII (Concluded)

BURNER TEST PLATE SAMPLES SUPPLIED TO REDSTONE ARSENAL

Ga. Tech Number	Composition	Fabrication Technique
11-12-A	33% fused silica (from slip) 16.8% -30+100 mesh fused silica grain 50.2% -100+325 mesh fused silica grain	Fused silica slip was gelled by adding 10 ml 2F NaOH solution and 15 ml saturated NH_4Cl solution to 800 ml of slip. Aggregate mixture was then added to gelled slip and mixed thoroughly, producing a thixotropic trowling mixture. Mix was cast in cardboard mold by vibration. Not fired.
11-12-B	Same as above	Same as above except fired at 1800° F for 16 hours.

The pure fused silica and fused silica and graphite samples were compared with graphite and Micarta samples under the same test conditions. The following table shows a comparision of the results:[6]

TABLE XIX

ABLATION OF FUSED SILICA AND GRAPHITE--FUSED SILICA SAMPLES TESTED BY GIANNINI RESEARCH LABORATORY

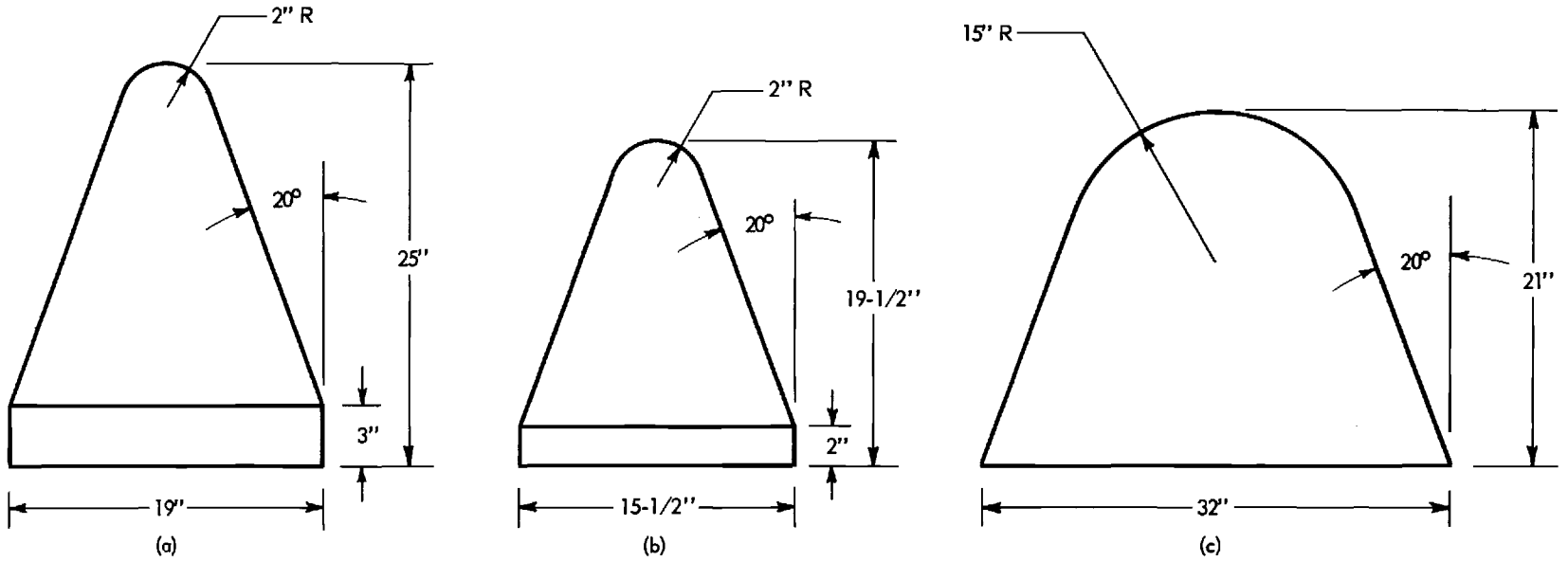
Material	Stagnation Point Ablation Rate (Cm/Sec)
Pure fused silica	0.050
Pure fused silica + graphite	0.044
National Carbon Grade ADR graphite	0.0133
Fiberglas Micarta 259-2	0.1014

The major conclusion reached from these tests was that fused silica (both with and without graphite) is a much better material than Fiberglas Micarta 259-2, at least as far as ablation is concerned. In general the pure fused silica stagnation point ablation rate is about one-half that of Fiberglas Micarta 259-2; the addition of graphite to fused silica lowers the rate still further. The stagnation ablation rate of pure fused silica is over 3.5 times that of graphite.

A large nose cone shell 25 inches in height, 19 inches in diameter at base, approximately 3/4 inch thick having a 3-inch straight section at its base shown in Figure 41(a) was easily slip cast in a plaster mold. The shell was fired for 2 hours at 2000° F in a gas kiln. Three mounting shoes were designed and fabricated for securing the nose cone shell on a mounting plate for mounting on test stand. The mounting shoes were secured to the inside of nose cone shell using Shell's Epon Adhesive VI. This nose cone shell was sent to Redstone Arsenal for evaluation.

A standard nose cone configuration, Figure 41(b), was slip cast to fit a metal liner supplied by ABMA. In casting, the metal liner was covered with a rubber cover and placed in the center of the plaster mold. The fused silica was allowed to cast from plaster to the rubber cover thus controlling the inside surface for controlled thickness. The cast nose cone shell was fired to 2000° F for 4 hours in a gas kiln. The metal liner was attached inside of the shell with Shell's Epon Adhesive VI and sent to Redstone Arsenal for evaluation.

A third large nose cone configuration shell, Figure 41(c), approximately one inch thick and having general dimensions of 32 inches in diameter at the base, 21 inches in height and a tip radius of 15 inches was slip cast in a



NOTE: DRAWING NOT TO SCALE

Figure 41. Large Nose Cone Configurations Sent to Redstone Arsenal.

plaster mold. The shell was fired in a gas kiln to 2000° F and held for 4 hours. This larger shape was formed so as to determine some of the fabrication problems that may be encountered in forming large shapes. No difficulty was encountered in forming this larger shape. This shell was sent to Redstone Arsenal.

V. CONCLUSIONS

A. Casting Fused Silica Grain

The grain sizes of fused silica and the binders studied were as follows:

-100 mesh as received (approximately 50 per cent -325 mesh)

-100+150 mesh

-150+325 mesh

-325 mesh

Colloidal silica

Clay

Lumnite cement

Hi-Early Portland cement

It was observed that colloidal silica, clay or Hi-Early Portland cement could be used as binders for fused silica grain to provide bars with modulus of rupture values in the 1000-to-1500-psi range. The clay and colloidal silica both required firing, whereas Portland cement provided an air set.

Clay and Portland cement had the least effect on lowering the melting point of silica, with colloidal silica having no effect. Lumnite had the greatest effect on the silica with only a 10-per-cent-addition lowering the melting point 200° F with a 20-per-cent-addition lowering it 400° F. Clay lowered the melting point only half this amount whereas Portland cement had almost no effect up to 20 per cent but increased rapidly above this amount.

Of the fused silica particle size distributions studied, the following ranges were established as providing the best compositions:

15 to 40 per cent	-100+150 mesh
30 to 55 per cent	-150+325 mesh
30 to 50 per cent	-325 mesh

This method of forming articles of high fused silica content was found to be most attractive for fabricating large and/or massive solid shapes. With the development of slip casting techniques now available it would not be recommended that casting grain be used as a method for forming nose cones. However, this casting technique might prove very desirable as a method for forming flame deflections or launching pads.

In an attenpt to form a casting slip of fused silica, the grain was ball milled with water and colloidal silica for various periods of times.

The most successful mill composition was as follows:

2000 gm -30+100 mesh fused silica

800 ml Ludox HS colloidal silica

6000 gm Burundum grinding cylinders

1 gal Porcelain mill

Milled for 24 hours

The modulus of rupture of bars cast from this slip was 2000 psi when fired at 1800° F for one hour.

Fused silica slip became available on a commercial basis from the Glasrock Corporation which exhibited superior casting properties over any yet prepared in the laboratory. Thus having large quantities of a consistently good slip available, further milling studies were abandoned.

Investigation of additives such as clays, powdered copper, iron-tin alloy, graphite, fiberglas, and phosphorous pentoxide were made to fused silica slips in an effort to develop techniques whereby compositions of fused silica may be tailored to fit some specific requirement for a re-entry vehicle.

It was found that clay additions up to 10 per cent were not detrimental to thermal shock resistance. Strength increases as great as three times were obtained with clay additions of only 5 per cent.

It was also established that heterogeneous bodies containing fused silica and copper, graphite or an iron-tin alloy could be slip cast. However, such bodies were too weak to be considered satisfactory.

The additions of fiberglas to the slip did not improve the strength above that of the pure slip. However, it was felt that much study was needed to establish the technique of dispersing the fibers properly through the slip and also the firing conditions required to prevent sintering of the fibers to themselves which increased the effective fiber diameter and thus reduced its reinforcing characteristics.

Phosphoric acid was added to the slip and also used to impregnate fired bodies in an effort to develop a silica-phosphate bond and thus improve the strength. Although strengths as high as 8000 psi were thus obtained, thermal shock resistance was reduced below an acceptable value. It was concluded the phosphorous pentoxide accelerated devitrification and that the large amount of cristobalite which was developed resulted in the high strength and low thermal shock resistance.

B. Dry Pressing of Fused Silica Grain

Dry pressing was investigated as a possible method for forming nose cones from fused silica grain.

The compacting of a nonplastic, brittle material such as fused silica grain is extremely difficult. Binder-lubricants, such as colloidal silica,

waxes, core oil and stearic acid; grain size distribution of the fused silica; and compacting pressure were studied in efforts to overcome compacting difficulties. None of these attempts were sufficiently successful in forming hardware, such as a nose cone, which could be used for re-entry vehicles. The composition which showed the greatest promise was fabricated from 60 per cent -325 mesh, 40 per cent -30+100 mesh fused silica grain; using one milliliter of Ludox LS colloidal silica per 10 gm of dry material; and a compacting pressure of 3,000 psi. The average transverse strength of this composition was 1094 psi; however the transverse strengths were inconsistent within a specified point studied, i.e., out of eight bars broken for this point the lowest value was 833 psi and the highest value was 1605 psi.

Because of the fabricating difficulties, high cost of dies and large presses needed to compact large objects, and since the slip casting of fused silica appeared to be so promising as a fabricating technique, the dry-pressing investigations were abandoned.

C. Fabrication of Large Nose Cones

Nose cones as large as 25 inches in height and 19 inches in diameter at the base, and nose cone tips as large as 21 inches in height and 32 inches in diameter at the base were easily fabricated from fused silica by the slip-casting technique.

The attachment of these nose cone shells to a metal insert or an attaching device was easily accomplished by the use of an adhesive such as Shell Epon Adhesive VI.

It is felt that there is no foreseeable size limitation in the fabrication of nose cones from fused silica. However, due to other problems such as furnaces, handling facilities and space requirements, there may be economical limitations above which size it may be desirable to fabricate nose cones in segments.

D. Thermal Conductivity Apparatus

An apparatus was constructed for determining the thermal conductivity of materials to a mean temperature of 2000° F.

The performance of the apparatus at temperatures above 1600° F indicates that no leakage to the thermocouples occurred. This is attributed to the low power requirements of the main heater, the increased thickness of the heater plate, and the insulation of the thermocouples in the surface of the main heater.

The results obtained with the one-quarter-inch sample of fused silica are not considered satisfactory since the temperature drop across the sample was small. The values measured with the one-half-inch samples should more accurately represent the temperature--thermal conductivity relationship for slip-cast fused silica. However, the measured thermal conductivity of this material is probably lower than the actual value due to the unsatisfactory surface finish of the samples. It is recommended that several samples of slip-cast fused silica which have been ground and lapped to ASTM specifications be tested in this apparatus in order to evaluate the error resulting from poor surface contact.

The operation of the apparatus was time consuming and difficult. This was primarily due to difficulties in balancing cold surface temperatures and

achieving steady state. This operation would be greatly enhanced by installing, in the auxiliary heater plates, circuits with more sensitive control than the powerstats.

E. Rocket Motor Test Facility

The Station's Ceramics Branch miniature oxyhydrogen rocket motor test facility was evaluated for use as a preliminary test device for screening various compositions to be tested by Redstone Arsenal's 4HT and 164HT burners. Comparison of data obtained for Micarta with Redstone Arsenal's facility and the Station's facility indicated that data obtained from the two facilities can be correlated. The maximum ablation rate obtained with the Station's facility was approximately one-half the maximum ablation rate obtained by Redstone Arsenal with their 4HT and 164HT burners.

Monofractions of fused silica grain mixed with water and Hi-Early cement exhibited ablation rates as high as 0.043 inches/second and as low as 0.004 inches/second. The compositions of these two ablation rates can be seen listed in Table VIII as samples K and G. It can be seen that a desired ablation rate within certain limits can be tailored from these compositions. It also should be noted that none of the compositions exhibited any backside temperatures.

Slip-cast fused silica fired at 2000° F soaked by prescribed standard methods with phosphoric acid and Shell No. 1310 Epon resin, were compared with a nonsoaked specimen. The phosphate-soaked specimen thermal shocked and the resin-soaked specimen exfoliated when subjected to the high temperature exhaust flame of the Station's facility. The unsoaked fused silica sample exhibited a slight bubbled surface and no measurable ablation after a 20-second run.

Additions of 3, 5, 10 and 15 per cent by weight of Microfyne and flake graphite to fused silica slip were made. From Table X it can be seen that the ablation rates of each composition were equal with the exception of the composition containing 3 per cent Microfyne graphite. The compositions containing Microfyne graphite exhibited the lowest change in backside temperature.

Thin shells, 1/8-to 3/16-inch, were cast from fused silica slips containing 1, 3, 5, and 10 per cent by dry weight of Microfyne and flake graphite. The shells were backed with slip cast fused silica slip. The smallest change in backside temperature was the laminate containing 5 per cent Microfyne graphite. This change in temperature was 19° C for a run time of 47.3 seconds. The graphite laminates exhibited better thermal-insulating properties and smaller changes in backside temperatures than the graphite additions to fused silica slip.

Copper laminates were fabricated in a similar method as the graphite laminates and using the same additions to the fused silica slip. The ablation rates of these samples were essentially the same except for the 5-per-cent-copper addition; it was 0.001 inch greater. This difference may be due to error in measurement. The change in backside temperature was less for the copper laminates than any of the graphites. A run time of 68 seconds exhibited a change of backside temperature of 14° C for the 10-per-cent-copper laminate. From Table XII it can be seen that the change in backside temperature becomes less as the copper addition increases.

An attempt was made to further lower the backside temperature by backing up thin shells of slip cast fused silica slip with fused silica foam. Small quantities of phosphoric acid were added to the foam when it was in a liquid state to improve its green and fired strength.

The addition of phosphoric acid affects the particle-to-particle bond and causes an increase in the heat-conducting properties of the material. This is indicated by the quick rise in backside temperature, Figure 37, curve C1, compared to the somewhat slower rise shown in curve A1.

The time required for a significant backside temperature increase of the foam laminates did not vary greatly from that required for a solid sample. This is explained by the fact that although the thermal conductivity of the foam is much lower than the solid body, the density is much lower also. Thus, the thermal diffusivity, $\frac{K}{\rho C_p}$, of the foam could be larger than that of the solid slip-cast material.

Respectfully submitted:

N. E. Poulos
Project Director

Approved:

J. D. Walton, Head
Ceramic Branch

Frederick Bellinger, Chief
Material Sciences Division

J. E. Boyd, Director
Engineering Experiment Station

VI. APPENDIX

A. Bibliography

1. Kingery, W. D., Ceramic Fabrication Processes. Technology Press of Massachusetts Institute of Technology, 1958, pp 45-51.

2. Jacob, Max, Heat Transfer. Vol. I, New York: John Wiley and Sons, 1959.

3. American Society of Testing Materials Standards, 1955, C177-45.

4. Dike, Paul H., Thermoelectric Thermometry, monograph for Leads and Northrup Company, Philadelphia 44, Pennsylvania.

5. McAdams, William H., Heat Transmission. New York: McGraw-Hill, 1954.

6. Interim Test Report, Ablation of Fused Silica Samples in Air. No. A-1 IR098-1313 for ABMA by Plasmadyne Corp., Santa Ana, California.

B. Source of Raw Materials

Binders

Colloidal Silica, Ludox LS, AS, SM and HS, E. I. DuPont de Nemours and Company, Inc., Grasselli Chemicals Department, Wilmington, Delaware.

Carbopole, B. F. Goodrich Chemical Co., 3135 Euclid Ave., Cleveland 15, Ohio.

Carbowax, Union Carbide and Chemicals Company, 41 Marietta St., N. W., Atlanta, Georgia.

Keltex, Kelco Co., 120 Broadway, New York 5, New York.

Clays

E. P. K. Kaolin, Edgar Plastic Kaolin Co., Edgar, Florida.

Kentucky Old Mine No. 4 Ball Clay, Kentucky - Tennessee Clay Co., Paris, Tennessee.

Electrolytes

Polyfon "O", Polychemical Division of West Virginia Pulp and Paper Company, Charleston, South Carolina.

Tennessee Air Extra, Tennessee Corporation, Atlanta, Georgia.

Fused Silica

Fused Silica Grain and Slip, The Glasrock Corporation, 1101 Glidden Street, N. W., Atlanta, Georgia.

Resins

Shell Epon 1310 Resin and Shell Epon Adhesive VI, Shell Chemical Corporation, New York, New York.

CTL-91-LD Resin, Cincinnati Testing Laboratories, 316 West Fourth Street, Cincinnati 2, Ohio.

Miscellaneous

Graphite, Joseph Dixon Crucible Company, Jersey City, New Jersey.

Powdered Copper, Metals Disintegrating Company, Inc., Elizabeth B., New Jersey.